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ONORANZE
AD
AMEDEO AVOGADRO DI QUAREGNA
NEL 1° CENTENARIO DELLA SUA MORTE

CONGRESSO INTERNAZIONALE
SULLE COSTANTI FONDAMENTALI DELLA FISICA
E
XLII CONGRESSO NAZIONALE DI FISICA

ORGANIZZATI

DALLA SOCIETÀ ITALIANA DI FISICA
SOTTO GLI AUSPICI E COL CONCORSO
DEL MINISTERO DELLA PUBBLICA ISTRUZIONE
DELL' UNIONE INTERNAZIONALE DI FISICA
DEL CONSIGLIO NAZIONALE DELLE RICERCHE
DELL' UNIVERSITÀ DI TORINO
E DEL COMITATO PER LE ONORANZE AD AMEDEO AVOGADRO

TORINO, 6-11 SETTEMBRE 1956

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La Direzione del Nuovo Cimento, licenziando questo fascicolo, desidera porgere al prof. R. DEAGLIO, Segretario generale dei due Congressi tenutisi a Torino in onore di A. Avogadro, e alla sig.na dott. MARIA VIGONE, il suo più vivo ringraziamento per l'aiuto dato nella organizzazione del fascicolo stesso.

Dagli scritti di Amedeo Avogadro

« L'hypothèse qui se présente la première à cet égard, et qui paroît même la seule admissible, est de supposer que le nombre des molécules intégrantes dans les gaz quelconques, est toujours le même à volume égal, ou est toujours proportionnel aux volumes ».

A. AVOGADRO, *Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps* - Juillet, 1811.

« Cette hypothèse consiste à dire, que les volumes égaux des substances gazeuses, à pression et à température égales, représentent des nombres égaux de molécules, ensorte que les densités des différens gaz sont la mesure des masses des molécules propres à ces gaz, et que les rapports des volumes dans les combinaisons ne sont que les rapports entre les nombres de molécules qui se combinent pour former des molécules composées ».

A. AVOGADRO, *Mémoire sur les masses relatives des molécules des corps simples* - Janvier, 1814.



Amedeo Avogadro

* Torino, 9 Agosto 1776

† Torino, 9 Luglio 1856

RENDICONTI DEI DUE CONGRESSI

P A R T E P R I M A

Discorsi celebrativi.

Discorso generale d'inaugurazione dei due Congressi.

G. POLVANI

Presidente della Società Italiana di Fisica

In questi giorni, nel prepararmi, così mentalmente, a ciò che in questa cerimonia di apertura dei due Congressi in onore di AMEDEO AVOGADRO avrei detto, una considerazione mi tornava spesso alla mente: quella cioè come in questi ultimi anni la nostra Società abbia preso occasione, nelle annuali riunioni nazionali e internazionali da essa stessa organizzate, di onorare la memoria di fisici italiani celebri dei quali ricorreva il centenario o della nascita o della morte — 1950: centenario della nascita di AUGUSTO RIGHI; 1954: centenario della morte di MACEDONIO MELLONI e quest'anno, 1956, centenario della morte di AMEDEO AVOGADRO — oppure momenti di particolare importanza per la Storia della Scienza nostra — 1949: centocinquantenario dell'invenzione della pila — o infine istituzioni scientifiche importanti per il nostro Paese — 1955: centenario della fondazione del giornale *Il Nuovo Cimento*.

E volgendo lo sguardo dal passato all'immediato futuro vedevo e vedo già profilarsi un altro centenario, anzi tricentenario imminente per l'anno prossimo, quello della fondazione dell'Accademia del Cimento, che certo non potrà essere dimenticato.

E questo desiderio di ricordare sia i nostri maggiori scienziati, sia i momenti di particolare importanza nella vita scientifica del nostro Paese, e al ricordo unire, quasi in dono o in offerta i risultati delle proprie ricerche dei propri studi, traevo le migliori testimonianze e il migliore auspicio per la serietà d'intenti che animano i nostri fisici, maestri ed allievi, gli uni o gli altri mossi, come sono, da egual viva passione nell'indagare il mondo che ci circonda. E, d'altronde, come meglio si può onorare la memoria di uno scienziato se non cimentandosi con opere in quella stessa disciplina — la Fisica per noi — dove egli eccelse e alla sua memoria queste dedicare? Ora è proprio per questo che oggi, sotto il nome di uno dei nostri antichi e celebri fisici — quello di AMEDEO AVOGADRO, cui tanto debbono la Fisica e la Chimica per il merito

ch'egli ebbe di scoprire quella legge che col suo nome sta a fondamento di tutta l'atomistica — oggi noi ci aduniamo per inaugurare due grossi e simultanei Congressi di Fisica, uno specializzato sulle costanti fondamentali e l'altro generale costituente un'ampia rassegna dell'attività svolta in questo ultimo anno dai Soci, specie italiani, della nostra Società di Fisica.

* * *

Chi non è addentro alle segrete cose della nostra scienza, si domanderà certo cosa siano queste costanti fondamentali, a che servano e perchè siano chiamate — per così dire — a partecipare attivamente, alle onoranze di AMEDEO AVOGADRO.

Alle prime due domande darà completa risposta tra un momento il professor DEAGLIO nella sua prolusione: alla terza domanda si permetta a me di risponder, direi, per dover d'ufficio.

La legge di Avogadro fa prevedere la possibilità d'introdurre nella Fisica un numero particolare che esprime quante molecole sono contenute in una opportuna quantità di ogni specie chimicamente definita. Se per ogni siffatta specie si assume come quantità quella che in grammi è espressa dallo stesso numero che esprime il peso molecolare, questo numero vale 602 486 quintilioni, numero spaventosamente grande quale si ottiene scrivendo diciotto zeri alla destra del numero 602 486. Questo numero — fermo restando la sua definizione — è fisso, è costante, cioè è sempre il medesimo, qualunque siano la specie chimica considerata e la complessità della molecola costituente la specie, vale a dire è il medesimo tanto se la molecola è costituita da un sol atomo, quanto se è costituita da centinaia e centinaia di atomi, come avviene nelle macromolecole della Chimica organica.

D'altra parte lo sviluppo della Fisica, soprattutto per ciò che riguarda i recessi più profondi della costituzione della materia, ha mostrato la opportunità, anzi la necessità d'introdurre altri numeri, altre costanti che hanno, come del resto quella tratta dalla legge di Avogadro, parte essenziale in tutta la fenomenologia strutturale. Tanto che la Fisica interpretativa delle strutture spesso si riduce in opportuni giuochi — si potrebbe dire — fatti con cotesti numeri e solo con cotesti numeri: circostanza meravigliosa questa che rende la nostra scienza quasi un'arte pitagorica.

Orbene, poichè la costante che scende dalla legge di Avogadro, quel numero cioè che sopra ho ricordato pari a 602 426 quintilioni, è la più antica nel campo strutturistico ed è sorta come tale (più antica veramente sarebbe, come conoscenza del valore numerico, quella della velocità di propagazione della luce, ma la sua partecipazione alla strutturistica è più recente di quella di AVOGADRO), così questa circostanza ci ha spinto a prendere, come tema del Congresso specializzato, quello delle costanti fondamentali, e a intitolarlo al nome del grande fisico torinese.

Da chi delle questioni relative alle costanti fondamentali si occupa in modo particolare, questa iniziativa è stata considerata — come confermano i consensi pervenutici — ottimamente opportuna, specie per quel che riguarda le costanti universali che delle fondamentali sono la parte, per così dire, più importante, una specie di *sancta sanctorum*, e ad esse appartiene appunto quella tratta dalla legge di Avogadro.

Il favore riscosso da questo Congresso è stato tale e tanto che noi pensiamo che ad esso — che è il primo del genere — potranno seguire negli anni futuri, non immediati però, un secondo, un terzo, e così via, tanta è l'importanza che queste costanti rivestono in tutta la Fisica

* * *

E pertanto siamo lieti e riconoscenti all'Unione Internazionale di Fisica, di aver voluto dare i suoi auspici e il suo patronato a questo Congresso; come siamo lieti e riconoscenti al Ministero della Pubblica Istruzione, al Consiglio Nazionale delle Ricerche, all'Università di Torino, al Comitato organizzatore per le onoranze di averci dato generosamente l'aiuto per quivi tenere e il Congresso specializzato e l'altro generale nazionale.

Lunga è la lista delle persone e degli enti cui dobbiamo la possibilità di questa duplice riunione ed io desidero qui farne esplicita memoria per additare le une e gli altri alla riconoscenza di tutti i nostri Soci, anzi di tutti i fisici dato che i risultati che da questa duplice riunione si trarranno, saranno per tutta la Fisica di notevole momento.

E anzitutto si rivolge la nostra gratitudine alla Città di Torino, così ospitale e nobile, e all'avv. AMEDEO PEYRON, degno suo rappresentante e Presidente del Comitato delle onoranze; al Consiglio Nazionale delle Ricerche e al Comitato per la Fisica e ai due Presidenti, l'Eccellenza il prof. COLONNETTI e il prof. PERUCCA, nostro nume tutelare presso di quello; all'Università e al suo Rettore prof. ALLARA; al Politecnico e al suo Rettore prof. CAPETTI; all'Amministrazione Provinciale di Torino e al suo Presidente prof. GROSSO; alla Società Fiat, e al suo Presidente, l'Eccellenza prof. VALLETTA, così tanto premurosamente sensibile ai problemi della cultura e della scienza; al conte MARONE CINZANO; alla Società Idroelettrica Piemontese e al suo Presidente avv. PACCES; alla Cassa di Risparmio di Torino e al suo Presidente prof. RICCALDONE; alla Società dell'Agip mineraria e al suo Presidente l'on. ing. MATTEI; alla Società Torinese Esercizi Telefonici e al suo Presidente prof. SOMEDA e al suo Direttore dott. RESI-ROMOLI; alla Direzione Generale per le Accademie e Biblioteche e al suo Direttore Comm. ARCAMONE; alla Società Cartiere Burgo e al suo Presidente MANSUETO RAVIZZA; alla Società Ferrania e al suo Presidente; alla Società Cogne e al suo Presidente Eccellenza gen. MARAZZANI; alla Società Snia-Viscosa e al suo Presidente Cavaliere del Lavoro,

MARINOTTI; alla Società Olivetti e al suo Presidente dott. ADRIANO OLIVETTI; all'Istituto Bancario San Paolo e al suo Presidente dott. CODA; alla Società Vetroteco e al suo Presidente avv. AGNELLI; alla Unione Industriale di Torino e al suo Presidente avv. GURGO-SALICE; alla Società Rumianca e al suo Presidente RICCARDO GUALINO.

Gli aiuti finanziari così generosamente offerti hanno valso per organizzare non solo i due Congressi ma, insieme a quelli pervenutici dalla Città di Como, dall'Editore dott. ALDO GARZANTI e dalla Unione Industriale di Bologna, ai quali ugualmente va la nostra gratitudine, hanno valso — dico — a rinnovare quella simpatica e proficua tradizione, che ormai da nove anni perdura vitale, dell'assegnazione di premi e borse a quei giovani o giovanissimi fisici italiani che maggiormente si distinguono nello studio della nostra disciplina. Ma di questa bella istituzione della nostra Società avrò occasione di parlare diffusamente martedì prossimo proprio alla chiusura del Congresso. Basti qui dunque l'accenno fatto.

Ma il denaro e i mezzi materiali messi a disposizione non sono tutto e di per sè sarebbero stati inoperosi se fosse mancata la collaborazione calorosa e premurosa in tutta la fatica della organizzazione.

E qui soprattutto al prof. DEAGLIO, impareggiabile Segretario Generale dei due Congressi e sicuro collaboratore, va il nostro più profondo e affettuoso ringraziamento; al prof. PERUCCA onnipresente e omnioperante direi e soprattutto carissimo amico; al prof. WATAGHIN cui dobbiamo non pochi spunti teorici per l'organizzazione scientifica, all'ammiraglio NOMIS DI POLLONE, alle collaboratrici del prof. DEAGLIO, particolarmente alla signorina dott. VIGONE, e ancora in altro campo al dott. NEPPI MODONA Capo Gabinetto del sig. Sindaco, al Direttore del Museo Egizio, al Direttore dell'Ente Provinciale del Turismo, a tanti e tanti altri, che certo ora mi sfuggono di mente: questi vogliano scusarmi e ascrivere l'omissione a sola involontaria dimenticanza, e anche se non nominati vogliano gradire ugualmente il nostro affettuoso ringraziamento.

Ma non basta. Di tutte le persone che in un modo o in un altro gravitano o hanno gravitato intorno a questa duplice riunione scientifica in onore di AMEDEO AVOGADRO, sono non ultimi attori, anzi direi i primi, gli scienziati qui convenuti. Di loro nominerò solo, e sono sicuro che tutti approveranno l'eccezione, il prof. BIRGE, emerito dell'Università di California e fondatore degli studi comparati sui valori più attendibili da assegnare alle costanti universali; il quale entusiasticamente accolse il nostro invito di partecipare al Congresso, e tanti consigli preziosi ci ha dato per ben organizzarlo. Egli tra poco prenderà la parola per un indirizzo alla memoria d'AVOGADRO.

E con lui sono venuti a Torino tanti altri, circa trecento, tra italiani e stranieri (e molti sono illustrazioni somme della nostra scienza), per alimentare

i due Congressi dei loro lavori, dei loro studi. A tutti il benvenuto e il ringraziamento della Società.

* * *

Da quanto ho detto risulta chiaro quanti interessi particolari e quanto interessamento generale abbia suscitato questa duplice riunione torinese; la quale, in fondo in fondo, se ben si guarda un solo scopo si propone: quello dell'avanzamento delle nostre conoscenze nel campo dei fenomeni fisici; puramente questo, direi.

Ed è veramente bella, profondamente commovente e di buon auspicio questa sete che tanti spinge a un medesimo fine, quello della pura conoscenza, ben sapendo tuttavia essi che ogni nuova conquista porta non a calmare questa sete, ma anzi a esasperarla, e a spingere più che mai verso l'ignoto rivelato dalla stessa conoscenza acquisita. È il nostro supplizio, la nostra pena questo di non poterci mai fermare sull'ultimo limite raggiunto e di dovere proseguire ininterrottamente su una via che è mistero dove ci porti. È la nostra pena, il nostro supplizio: forse la nostra salvezza.

Ma non lasciamoci prendere la mano dalla fantasia o dalla malinconia o dal voler saper troppo. Stiamo al dunque e torniamo ai nostri due Congressi.

E poichè già troppo ho parlato e troppo ho fatto a tutti attendere di ascoltare le parole del prof. DEAGLIO nella sua prolusione, chiuderò il mio dire con la rituale dichiarazione di apertura dei due Congressi, con l'invito al lavoro e con l'augurio certo di proficuo successo.

La vita e l'opera di Amedeo Avogadro.

E. PERUCCA

Istituto di Fisica del Politecnico - Torino

Di AMEDEO AVOGADRO, chimico-fisico di quando la chimica fisica era scienza non ancora nata, parlerò rievocando di Lui la vita e dei suoi studi quelli che più si attengono alla fisica.

Di questi ultimi fanno fede gli scritti che ritengo siano tutti a nostra conoscenza. E allora oserei dire che il compito è facile.

Dell'altra pochi elementi sono sicuri, sicchè considero piuttosto fallita l'impresa di scrutar l'Uomo attraverso il microscopio dei suoi sentimenti più gelosi perchè più veri.

Questo scienziato percorse degna e lunga parabola di vita; ma sono nulle o ancora nascoste le tracce che ne delineino l'intima figura.

Fu modesto e fin quasi schivo per concorde testimonianza di quanti lo conobbero.

Fu tutto dedito alla famiglia, una non lieve famiglia che giunse a otto figli; e nessuna altra sua passione si conosce oltre quella degli studi scientifici.

L'illustre casata e qualche parola tratta da una ormai antica celebrazione mi indussero a immaginare un piccolo AMEDEO in velluto nelle lussuose sale di una torinese residenza patrizia, in attesa di essere maturo per calze di seta e spadino di Corte.

Troppi altri indizi mi convincono che l'immagine era del tutto retorica e il ritratto del fanciullo, del giovane sfuggito a Themis per sacrificare a Minerva, si perde nella nebbia delle congetture.

Figlio di FILIPPO, nominato conte nel 1787 da VITTORIO AMEDEO III per le qualità davvero eccellenti dimostrate quale altissimo funzionario dello Stato, AMEDEO apparteneva ad una nobiltà piemontese di antica origine, riconosciuta per recenti meriti ed altamente onorata da lui, dai suoi fratelli, dai suoi discendenti.

Un buono stipendio del Padre, che nel 1795 fu di lire 4000 annue ⁽¹⁾ con altri « proventi sul lavoro » garantiva una distinta ma non doviziosa situazione familiare ⁽²⁾.

In quanto alla casa ove AVOGADRO nacque in Torino, l'ho cercata invano ⁽³⁾. Essa era certo nell'ambito della Madonna del Carmine, probabilmente presso l'antica Porta Susina, dove il profondo rinnovamento urbanistico di Torino nel primo Ottocento nulla deve aver concesso a cimeli che, evidentemente, poco contavano per l'arte e la cui scomparsa soltanto a noi suscita rimpianto ⁽⁴⁾.

In questa casa ignota LORENZO ROMANO AMEDEO CARLO AVOGADRO, il nostro AVOGADRO nacque il 9 Agosto 1776 e il giorno dopo fu battezzato nella chiesa del Carmine.

Niente calze di seta e spadino, ma più verosimile è qualche sculacciata sia pur patrizia, e seguirono poi, quando fu giovinetto, i rabbuffi materni per certe invasioni sui fornelli di cucina ove AMEDEO, forse col fratello FELICE di due anni minore, stuzzicava il calorico per vederne gli effetti. Così si racconta.

Se, però, documenti vogliamo e non congetture, siamo fortunati nei registri universitari di Torino: AMEDEO il 5 Dicembre 1795 prende la « licentia » in diritto e il 16 Marzo 1796, non ancora ventenne, è laureato in ambe leggi (ecclesiastica e civile).

Subito dopo egli è nominato Avvocato dei Póveri; anche per lui si apre la strada giuridica così valentemente seguita dal padre, conforme alla tradizione e al nome stesso della casata ⁽⁵⁾.

Lo segue a ruota il fratello FELICE, divenuto anche lui dottore in ambe leggi.

Siamo alla fine del secolo e fortissimi furono in quegli anni i rivolgimenti scientifici: chimica e fisica sono sovvertite dalla conservazione della materia di LAVOISIER, dalla corrente elettrica di VOLTA.

Che più naturale della passione dei due dottori in ambe leggi per le nuove scienze? Sì, la passione ci fu. Ma non è su AMEDEO AVOGADRO che possa scriversi una storia romanzata; al più qui ve n'è un piccolo spunto.

Sono gli anni di Napoleone e della Repubblica Cisalpina, anni « caldi » per tutti, anche per la giovane, ma già autorevole Accademia delle Scienze di Torino.

⁽¹⁾ I professori titolari meglio pagati dell'Università di Torino raggiungevano allora le lire 2000 annue.

⁽²⁾ Anche il conte FILIPPO ebbe otto figli; AMEDEO fu il terzo ed il secondo dei maschi.

⁽³⁾ Per questo ed altro a molti ho chiesto e devo aiuto; V. nota ⁽⁴¹⁾.

⁽⁴⁾ Abiterà poi AMEDEO, con la sua famiglia, dal 1829 fino alla morte in un alloggio, anche esso scomparso, al 3° piano di n. 49 in Dora Grossa, quasi sul posto ove è il n. 49 dell'attuale Via Garibaldi.

⁽⁵⁾ AVOGADRO da « advocatus ».

A seconda del vento che spira, l'Accademia chiude i battenti, li riapre mutando e ancor mutando nome; l'invito di allora è acclamato presidente onorario...; insomma sono le solite cose.

A questa Accademia (pel momento Académie des Sciences, Littérature et Beaux-Arts) il 20 Settembre 1803 è presentata una nota dal titolo: *Essai analytique sur la nature du fluide électrique*; l'Accademia, secondo norma, nomina una Commissione di esame nei Soci B. C. BONVOISIN (BONVICINO) e A. M. VASSALLI EANDI, e il primo, a nome di entrambi, riferisce nella seduta accademica del 25 Novembre successivo:

« Les rapporteurs croient que la théorie adoptée par les jeunes Auteurs du mémoire, qui déclarent être les citoyens Aimé et Félix Avogadro, n'est pas entièrement appuyée, mais qu'il mérite des éloges et une mention honorable dans l'histoire » ⁽⁶⁾.

La memoria, non pubblicata, scritta di mano di AMEDEO, è, ancor oggi, negli archivi accademici.

Da questi si può sicuramente individuare la disapprovazione accademica nelle troppo immaginose idee degli autori sulla possibilità di identificare il fluido elettrico col fluido calorico.

Ma mi sorprende che negli stessi verbali accademici, qualche pagina dopo si annoti:

« Les Proff. R... e G... ⁽⁷⁾, en substituant dans la formation de la pile [di VOLTA] des disques de chair cancéreuse et de viande putride à ceux de carton mouillé, et faisant agir cette pile sur une solution de nitrate d'argent moyennant des fils d'or, ont conclud, des flocons noirs qu'ils ont observé, que les miasmes putrides de la viande dont ils avaient formé la pile, avaient passé par les conducteurs et agi sur la solution.

Le Prof. R. a aussi essayé les secousses de ces piles à la langue, et il a eu des vomissements. »

Dobbiamo al *Journal de Physique* di Parigi, detto « di de La Métherie » se le fantasticherie giovanili degli AVOGADRO sono pubblicate, sicché prendono data e sono consegnate ai fisici di allora e di oggi ⁽⁸⁾.

Le due parti sono al nome del solo AMEDEO; la collaborazione di FELICE è ricordata solo in una nota. È dunque evidente la posizione preminente di AMEDEO.

⁽⁶⁾ Effettivamente i due AVOGADRO furono di conseguenza nominati Soci Corrispondenti dell'Accademia.

⁽⁷⁾ Entrambi Soci Effettivi dell'Accademia.

⁽⁸⁾ La memoria è divisa in due parti: « Considérations sur l'état dans lequel doit se trouver une couche d'un corps non conducteur de l'électricité lorsqu'elle est interposée entre deux surfaces douées d'électricité de différente espèce » in *Journ. de Phys. de La Métherie*, 63, 450 (1806), e « Second memoire sur l'électricité, ou suite des considérations sur l'état etc... », in *Journ. de Phys. de La Métherie*, 65, 130 (1807).

Ebbene: all'autore di questa memoria deve, sì farsi l'appunto di immaginare l'intervento del fluido calorico negli affari elettrici fino a porre la domanda se fluido elettrico e fluido calorico non siano per caso identificabili ⁽⁹⁾.

Su ciò gli Accademici di Torino ebbero buon motivo di esprimere un giudizio non favorevole; ma ciò infirma, se mai, solo la seconda parte della memoria, e sol nei punti ove quella supposizione appare.

Allo stesso tempo cosa fu perduto per noi! Lo dirò con le stesse parole di AVOGADRO:

«Voilà donc l'idée que les faits nous ont conduit à nous former de toute couche isolatrice, ... prise entre deux électricités d'espèce contraire; c'est qu'on doit la concevoir comme formée d'une infinité de couches, qui toutes, quelque minces qu'elles soient, offrent sur leurs surfaces opposées deux électricités d'espèce contraire, de même que l'assemblage qui en résulte. »...

«Nous avons donc là une modification particulière qui a lieu dans toutes les molécules d'une couche d'air interposée entre deux corps qui s'attirent par leur électricité contraire.... Il me semble difficile de ne pas admettre que cette modification, qu'elle qu'en soit la nature intime, est le moyen par lequel l'attraction s'opère, puisque il ne paroît pas convenable d'admettre une autre force que l'attraction universelle, qui agisse à distance entre électricités contraires ».

Fu perduta l'ipotesi della polarizzazione dielettrica e l'ipotesi dell'azione del mezzo in luogo dell'azione coulombiana a distanza.

Sia la prima ipotesi, già abbozzata dal HAÛY per la piroelettricità della tormalina e dal COULOMB per le calamite, sia la seconda ipotesi, entrambe stampate su di un giornale di alta autorità, verranno tuttavia ignorate; ipotesi per allora immature, solitarie, sterili, saranno riprese trenta anni dopo da M. FARADAY e da O. F. MOSSOTTI che rivendicherà per AVOGADRO la priorità ⁽¹⁰⁾.

Immagino quale incentivo a perseverare sulla via della fisica venne agli AVOGADRO dalla pubblicazione della loro memoria. Ma che delusioni li attendono!

⁽⁹⁾ Come curiosità ricordo che oltre 40 anni dopo, per un momento, J. P. JOULE propose il connubio tra carica elettrica in rotazione nella molecola e calore.

⁽¹⁰⁾ MOSSOTTI attribuisce all'AVOGADRO perfino il principio delle superficie corrispondenti dell'elettrostatica; a me pare che questo principio sia, infatti, insito in tutte le considerazioni dell'AVOGADRO, ma sotto forma ancor piuttosto qualitativa; l'elettrostatica quantitativa non poteva dirsi ancor nata.

Non vorrei, poi, sopravvalutare oggi nè le idee di AVOGADRO nè quelle di FARADAY-MAXWELL per ciò che riguarda il problema dell'azione a contatto e dell'azione a distanza; dopo il sommovimento di un secolo fa, questo problema mi sembra sopito nella fisica recente. D'altronde sia AVOGADRO, sia FARADAY trent'anni dopo, sembrarono ignorare ciò che BOYLE (1687) già sapeva e cioè che le azioni elettrostatiche si trasmettono anche nel vuoto; ora la polarizzazione dielettrica del vuoto è un palliativo del secolo scorso, ormai messo in soffitta.

Altre due successive memorie di fisica presentate all'Accademia di Torino ricevono altre due « menzioni onorevoli », ma niente pubblicazione. Nè queste memorie furono pubblicate altrove.

Nella prima delle due memorie di fisica si segnalano casi nei quali non è soddisfatta una regola proposta da BIOT e ARAGO per dedurre per un composto un certo « *pouvoir réfringent* », da essi definito, quando sia noto quello dei componenti.

L'altra memoria, sulla distribuzione dell'elettricità alla superficie dei corpi conduttori, presentava obiezioni alla legge di COULOMB che, come si è visto, non era gradita agli autori perchè legata all'azione a distanza. Forte del senno di poi, posso immaginare che le obiezioni fossero tutte a lor volta confutabili; ma la tirata d'orecchi, con cui questa volta l'Accademia di Torino (30 marzo, 1811) accompagnò la menzione onorevole e l'invio dello scritto agli archivi, non riguarda questa confutabilità, bensì una... mozione d'ordine: « una scienza come quella che [gli autori] coltivano e con successo, ammette congetture o ipotesi sol dopo che una folla di fatti sicuri e sperimentati si riveli contraria alla interpretazione [dominante] dei fatti ».

In verità, su questo punto c'è stata una forte rivalutazione: oggi basta un fatto « sicuro e sperimentato » a richiedere « nuove congetture e ipotesi ».

Ed ancora una quarta memoria dei fratelli AVOGADRO subisce la stessa sorte: altra menzione onorevole, accompagnata in questo caso da elevate parole di lode del Socio relatore GIOBERT, ma niente pubblicazione ⁽¹¹⁾.

Questa volta non sono più sculacciate patrizie per il nostro AMEDEO, ma sculacciate accademiche!

In mancanza di documenti, lasciatemi indulgere alla fantasia: deve esserci stata una « spiegazione » tra i due fratelli, e saran corse parole serie.

« Lo vedi che succede a far l'altrui mestiere? Chi ce lo fa fare di abbandonare ambo le leggi che tanto sono nella tradizione nostra, nelle quali tanto si è illustrato nostro padre Conte Filippo », avrà detto FELICE, meno inquinato dalle nuove scienze.

Avrà risposto AIMÉ: « Ho ben fatto l'avvocato e non in un posto solo ⁽¹²⁾; ma ormai nutro altr'esca; ho lasciato il posto in Prefettura per essere « *Répétiteur de physique* » ⁽¹³⁾, ho accettato la nomina di direttore e professore di « filosofia positiva » al Collegio di Vercelli ⁽¹⁴⁾; questa è ormai la mia strada ».

⁽¹¹⁾ La memoria, di contenuto chimico, è conservata negli archivi dell'Accademia di Torino.

⁽¹²⁾ Dopo l'Ufficio dei Poveri passò all'Avvocatura Generale, che era la palestra che in generale preludeva all'Alta Magistratura; indi passò all'Ufficio di Prefettura del dipartimento dell'Eridano.

⁽¹³⁾ Al Pensionnat de l'Académie; in quegli anni questo era il nome del Collegio delle Provincie.

⁽¹⁴⁾ Cioè di « fisica »; il « Collegio » di Vercelli è, poi, il liceo; vi fu nominato nel 1809.

« Ebbene sia; tutto è finito » tra noi » avrà concluso FELICE, pensando (si capisce) alle scienze nuove.

Sta il fatto che non si ha più traccia di collaborazione tra i due, e trovo FELICE nel 1814 avvocato fiscale a Susa, nel 1832 prefetto a Vercelli; egli sarà poi senatore del Regno Sardo.

Sta il fatto che per molti anni non vi è più traccia di memorie di AVOGADRO all'Accademia delle Scienze di Torino, e la grande memoria che si inizia con l'immortale ipotesi di AVOGADRO ⁽¹⁵⁾ emigra anch'essa, come le due prime sulla polarizzazione dielettrica e sull'azione del mezzo, al *Journal de Physique* di de La Métherie ⁽¹⁶⁾.

Così AVOGADRO, cui piacerà varie volte nella sua vita ⁽¹⁷⁾ dichiararsi un fisico, ma che già si era affacciato al campo della chimica con un lavoro pubblicato anch'esso in Francia nel 1809, vi entra Maestro per lunghi anni ignorato o incompreso, e con LAVOISIER, DALTON, PROUST, GAY-LUSSAC scrive le tavole della nuova scienza.

Qui esco di strada perchè LUIGI ROLLA, nostro decano insigne di chimica.

⁽¹⁵⁾ « M. GAY-LUSSAC a fait voir dans un mémoire intéressant (*Mémoires de la Société d'Arcueil*, tome II) que les combinaisons des gas entre eux se font toujours selon des rapports très simples en volume, et que, lorsque le résultat de la combinaison est gazeux, son volume est aussi en rapport très simple avec celui de ses composants; mais les rapports des quantités des substances dans les combinaisons ne paroissent pouvoir dépendre que du nombre relatif des molécules qui se combinent et de celui des molécules composées qui en résultent. Il faut donc admettre qu'il y a aussi des rapports très simples entre les volumes des substances gazeuses, et le nombre des molécules simples ou composées qui les forme. L'hypothèse qui se présente la première à cet égard, et qui paroît même la seule admissible, est de supposer que le nombre de molécules integrantes dans les gas quelconques, est toujours le même à volume égal, ou est toujours proportionel aux volumes.

En effet si on supposait que le nombre des molécules contenues dans un volume donné fût différent pour les différens gas, il ne serait guère possible de concevoir que la loi qui présiderait à la distance des molécules pût donner, en tout cas, des rapports aussi simples que les faits, que nous venons de citer, nous obligent à admettre entre le volume et le nombre des molécules ».

Secondo alcuni, AVOGADRO sarebbe giunto alla sua ipotesi, che stabilisce una proprietà comune ai gas, confortato anche dal fatto della uguaglianza della loro dilatazione termica. È sicuro che AVOGADRO dalle pagine di GAY-LUSSAC apprese la legge di Charles - Gay-Lussac. È molto probabile che al suo spirito sottile quest'ultima abbia dato da pensare. Ma non ho prove definite che egli sia stato condotto alla sua ipotesi dalla legge di dilatabilità e da quella dei volumi insieme. Osserverò infine che la locuzione « molecules integrantes, » usate da AVOGADRO, deriva dall'HAÛY che se ne serve nella sua descrizione della struttura dei cristalli; le « molecole integranti » di AVOGADRO sono le molecole nel significato attuale.

⁽¹⁶⁾ Vol. 73, pp. 58-78 (1811).

⁽¹⁷⁾ V. per es., *Mém. R. Acc. Sc. Torino*, 26, p. 2 (1821).

fisica, ha parlato ieri a Vercelli dell'opera di AMEDEO AVOGADRO nella chimica.

Era difficile non uscirne parlando di una legge che non soffre gerarchie nell'appartenere con pari, somma autorità all'una e all'altra scienza; ma rientro nei miei limiti, la fisica.

AVOGADRO sentì subito l'importanza della sua ipotesi per la chimica ed a questa si dedicò precipuamente. Ma non mancano tra le ricerche di AVOGADRO, che proseguiranno per ancora un quarantennio variamente alternandosi, quelle a carattere strettamente fisico. Tali sono le ricerche vercellesi del 1816-17, che poi proseguono ancora nel 1819-20, costituenti un primo gruppo di lavori sulla termologia: calori specifici dei gas, calori di reazione, leggi di dilatazione dei liquidi, densità, tensioni di vapore.

Sull'argomento dei calori specifici egli ritorna e ritornerà ancora a più riprese dopo la nomina all'Università.

Miseri erano i suoi mezzi sperimentali e spesso immature le questioni che egli prendeva a trattare.

Se non c'è molto da trarre da tali lavori per la fisica di oggi, interessa però segnalare come in tutti questi lavori si riveli il caratteristico spirito di AVOGADRO nello studio scientifico: la ricerca del coordinamento dei fatti, ossia delle leggi nella natura, più che la ricerca del fenomeno nuovo.

Interessa però segnalare che AVOGADRO va ricordato insieme con F. E. NEUMANN per i tentativi (1831) di estensione ai composti della regola di DULONG e PETIT sui calori atomici (1819), e che ad AVOGADRO si deve fare alto merito per le sue determinazioni del calore specifico del carbonio, di dieci anni anteriori eppur praticamente coincidenti con quelle di REGNAULT; molto si valse AVOGADRO di queste determinazioni per discuterne l'eccezione alla legge di DULONG e PETIT di allora.

Se molto di quanto egli scrisse è in oblio, io devo ricordare quali brutti anni passarono allora i fisici che si dedicarono al « calorico » ed ai calori specifici dei gas.

In generale i primi decenni del secolo scorso furono anni di crisi, come tanto spesso si parlò di « crisi della fisica » un secolo dopo.

La disfatta del flogisto può fissarsi al 1789 ⁽¹⁸⁾, e AVOGADRO fu salvo. Ma il fluido « calorico » fu l'angelo nero della fantasia scientifica del Nostro e non di lui soltanto.

Il calorico fu detronizzato lui vivente, ma non scomparve subito ⁽¹⁹⁾.

Al « calorico », nome che fu duro a morire, si sovrapposero la conservazione dell'energia e la termodinamica.

⁽¹⁸⁾ A. L. LAVOISIER: *Traité élémentaire de chimie etc.*, 2 voll., (Paris, 1789).

⁽¹⁹⁾ Nel prezioso *Dictionnaire Universel du XIX^e Siècle* di LAROUSSE, 3^o volume, 1867, alla voce « chaleur » trova già autorevolissimo posto la « teoria meccanica del calore », ma si legge che ancor la grande maggioranza dei fisici era pel fluido calorico.

Allato divampò l'elettrologia, l'ottica ondulatoria.

Non fu dunque lieve la crisi della fisica di allora.

E questo calorico, angelo nero, aveva davvero un carattere diabolico; e si divertì a scherzi bizzarri.

Che scherzo fosse quello fatto agli AVOGADRO nella loro prima memoria l'ho detto.

Il calorico concesse a DULONG e PETIT di trovar la loro fondamentale regola sul calore atomico degli elementi solidi; poco dopo concesse a N. L. SADI CARNOT di scrivere le sue mirabili *Réflexions sur la puissance motrice du feu* (1824).

Concesse a CLÉMENT e DESORMES (1819) di stabilire il concetto di « zero assoluto » con argomenti che si ripetono ancor oggi perfino nella fisica elementare. Ma in che ginepraio li mise, ancor ignari di calori specifici dei gas a pressione o a volume costante, con la loro classica esperienza di espansione dei gas, la quale appunto di quei calori specifici determina il rapporto. Gli autori credevano che quell'esperienza li conducesse a determinare il « calore specifico del vuoto ».

E fu il calorico a trascinar GAY-LUSSAC, uno degli ingegni più insigni e fecondi dell'epoca, a sostenere (1818) che ogni temperatura, comunque bassa, è possibile.

* * *

Il 19 Settembre 1819 AVOGADRO rinuncia all'insegnamento vercellese; secondo I. GUARESCHI era già sicura la sua nomina a professore di « fisica sublime » ⁽²⁰⁾; certamente egli ha già affermato la sua autorità scientifica al punto che subito dopo (21 Novembre 1819) è nominato Socio effettivo di quella Accademia delle Scienze di Torino presso la quale non erano stati proprio rosei gli inizi, ma alla quale Egli si dimostrerà poi profondamente affezionato.

Nell'anno scolastico 1819-1820 svolge certi gruppi di lezioni all'Università e la nomina, preannunciategli ufficialmente il 22 Luglio 1820, è perfezionata con Lettera Patente di S. M. (VITTORIO EMANUELE I) con la data del 6 Novembre di quell'anno.

Poco dopo, nel 1821, AVOGADRO è nominato Socio della Società Italiana detta « dei XL ».

Quarantacinquenne, può finalmente trovarsi in un centro di studi superiori, avrà un gabinetto sperimentale universitario; non può mancare il frutto agli studi che subito intraprende. E infatti sono del 1821 due poderose memorie entrambe inserite nei volumi dell'Accademia di Torino; riguardano la sua « ipotesi », l'importanza di essa per la chimica e la portata sempre più ampia.

Il 20 Gennaio 1822 AVOGADRO annuncia all'Accademia la costruzione di

(20) Qualcosa tra la fisica superiore e la fisica teorica, la fisica matematica di oggi.

« uno strumento atto a indicare l'esistenza e misurare la forza delle più deboli correnti voltiane », e il 21 Aprile successivo presenta una memoria su tal « strumento » e « sur son application à la détermination de l'ordre des métaux relativement à leur électricité par contact » ⁽²¹⁾.

Questo lavoro, a cavallo tra la fisica e la nascente elettrochimica, il primo di AVOGADRO sulla corrente elettrica, merita ben più che le alcune parole cui devo qui limitarmi.

Nuovo lo strumento, costruito sul principio del « moltiplicatore » di Schweigger appena comparso; nuova e feconda l'applicazione e cioè il controllare « l'ordre que gardent entre eux les différens métaux dans l'électricité positive ou négative qu'ils prennent par leur contact mutuel, ou du moins relativement au sens du courant voltaïque qu'ils excitent par l'addition d'un conducteur humide ».

Sono parole scritte all'inizio del 1822, a due anni di distanza dalla scoperta di OERSTED, e il loro stile esatto non è da meno di quello delle migliori pagine di VOLTA.

La serie dei metalli data da AVOGADRO si sostituisce con vantaggio a quella già nota di VOLTA e che potremmo dire elettrostatica, esente da conduttori umidi, ed a quella di RITTER che di questi ultimi fa uso e la rana è galvanometro.

Egli osserva pel primo alcuni casi di mutamento del verso della corrente con la variazione della sola concentrazione del « conducteur humide » (acido più o meno diluito) e indica pure alcuni casi in cui non vi è identità tra la serie di VOLTA (ove i metalli sono « eccitati per contatto », cioè si usa il metodo che noi abbiamo detto elettrostatico), e la sua serie basata sul verso della corrente ottenuta col conduttore umido.

E scrive: « celà nous conduit naturellement à accorder à l'action chimique... une influence que la théorie de Volta lui refuse puisque elle attribue toute la faculté électromotrice au contact des métaux ».

I fatti segnalati da AVOGADRO avrebbero dovuto da soli far tacere la polemica allora in fiamme sulla localizzazione delle differenze di potenziale al contatto; invece anche questa bella memoria di AVOGADRO, pur largamente citata, ad esempio, nel trattato di WIEDEMANN, non ebbe la risonanza che meritava.

Ma all'alba universitaria radiosa ecco succedere un opaco destino.

Tra i provvedimenti repressivi, dopo i moti del 1821, il re CARLO FELICE, con decreto del 24 Luglio 1822, sopprime alcune cattedre universitarie ⁽²²⁾ tra le quali è quella di « fisica sublime ».

⁽²¹⁾ *Mém. R. Acc. Sc. Torino*, 27, p. 43 (1823); ivi sono anche segnalati i primi fenomeni di quella che fu poi detta « passività ».

⁽²²⁾ E sono anche soppresse l'Azienda Economica dell'Università e il Collegio delle Provincie.

« Il Sig. Cav. AVOGADRO avrà a godere dell'annuo trattenimento di L. 600 sulla Cassa dell'Università, sino a che sia destinato ad altro impiego ».

Due anni dopo (3 Aprile 1824) gli è confermato l'annuo trattenimento di L. 300 che gli erano state assegnate come pensione per l'insegnamento di Vercelli. Se ho ben compreso, solo allora si giunge a L. 900 annue in tutto ⁽²³⁾.

Ma di lì a qualche mese AVOGADRO è nominato Mastro-Uditore sedente in Magistrato nella Reale Camera dei Conti, carica di cui nello stesso 1824 divenne titolare e che tenne poi per tutta la vita.

È noto quali colpe macchiassero l'*Alma Mater* di Torino: nei suoi giovani fu il fermento delle « prime spliè », le prime scintille ancor solo vagamente consapevoli del risorgimento.

È men chiaro quanta parte di queste onorevoli colpe gravassero sul professore di « fisica sublime », che ci è facile immaginar col cervello pieno di molecole integranti, ci è difficile immaginar nelle vesti del cospiratore. Sembra sicuro che molto caldo non fosse per l'autorità costituita di allora, ma le ispezioni fatte per l'occasione lo dichiararono esente da connivenze.

Un beffardo destino lo volle coinvolto, vittima, in una rappresaglia dalla quale non lui certamente esce bollato dalla storia.

Sarà questo il momento nel quale l'uomo AVOGADRO, cacciato dal « suo » posto, con un misero « trattenimento », già con quattro figlioli al sole e il successivo non ancora, si rivelerà meglio a noi?

No.

Dell'uomo a cui non sembra grave lo scrivere, sicchè ben settantacinque volumi di circa settecento pagine cadauno, in innumerevoli quaderni vergati di suo pugno si conservano rispettosamente raccolti alla nostra Biblioteca Civica, non abbiamo in qualche lettera, in qualche suo appunto un cenno che amarezza, scoraggiamento, irritazione, ribellione lo invadano, o almeno alberghino in lui.

Se scritti privati, se un epistolario di AMEDEO AVOGADRO esistono, essi sono tuttora ben ignorati; d'altronde troppo raccolta fu la sua vita, troppo tacita la sua morte, troppo tardo il suo riconoscimento, perchè io osi sperare ancor fruttuosa la ricerca dello storico, e mutevole il ritratto di AVOGADRO.

Tolto alla cattedra, divenuto Mastro-Uditore, egli può ancor rimuginar fisica e chimica con i Colleghi Accademici. Così il dodicennio di sospensione dalla cattedra (tanto durerà il suo esilio universitario) non indica alcun segno di diminuita attività di studi e le pubblicazioni che egli ne trae non danno segno di abbandoni o di scoramenti.

La restituzione alla sua cattedra avviene infine con nomina del 28 No-

⁽²³⁾ Dai documenti potuti trovare risulta che AVOGADRO, ancor nel 1838, ripreso l'insegnamento universitario, percepiva la pensione vercellese.

vembre 1834, di re CARLO ALBERTO, una nomina prudentissima, per « l'insegnamento provvisorio, finchè venga da noi altrimenti disposto » ⁽²⁴⁾.

Ma intanto uno dei periodi più pieni, più operosi per l'uomo di scienza è trascorso. AVOGADRO è quasi sessantenne.

Ebbene questo patrizio, che « fu di costituzione delicata », non torna alla cattedra per recitarvi un vuoto « hic manebimus optime ».

Riprende antichi argomenti di studio, ai quali non si stanca di aprir nuove vie. E ne abborda di nuovi come quello sulla capillarità ⁽²⁵⁾, notevole per gli abili artifici sperimentali con cui supera le difficoltà d'impiego di tubicini di sostanze opache e notevole per la chiara disamina di talune situazioni non ancora studiate, come ad esempio la capillarità alla superficie di contatto di due liquidi.

Ma specialmente va ricordata di questo periodo la sua poderosa *Fisica de' corpi ponderabili* ossia *Trattato della costituzione generale dei corpi*.

Quattro grossi volumi ⁽²⁶⁾, in lingua italiana, di quasi mille pagine ciascuno.

La dedica si inizia così: « L'opera che io oso offrire a V. M. [re CARLO ALBERTO] è frutto degli incoraggiamenti che la Maestà vostra e i suoi Reali Predecessori hanno compartiti ai deboli miei sforzi per cooperare al progresso delle Scienze Fisiche in questi Regi Stati ».

Allo storico già invocato, lascio il compito di indagare se queste parole van poste in relazione con altre successive della stessa dedica sulla munificenza di S. M. ⁽²⁷⁾.

⁽²⁴⁾ È ancor del 10 Dicembre 1848 la proposta del Consiglio universitario al Magistrato della Riforma perchè AVOGADRO sia nominato Professore effettivo. Secondo quanto ho potuto finora rintracciare, non risulta che la proposta abbia avuto seguito.

⁽²⁵⁾ Memoria letta all'Acc. Sc. Torino il 10 Luglio 1836 e pubblicata in *Mem. R. Acc. Sc. Torino*, 40, 191 (1838).

⁽²⁶⁾ Pubblicati a Torino, presso la Stamperia Reale: il 1° nel 1837, il 2° nel 1838, il 3° nel 1840, il 4° nel 1841.

⁽²⁷⁾ Alla pagina seguente la dedica continua, infatti, con queste parole: « Compiuto ora questo lavoro, e venuto ad acquistar forma acconcia, secondo mi parve, a rappresentare la somma di questa parte delle cognizioni fisiche, io mi fo animo ad umiliarlo a V. S. R. M., omaggio ben dovuto a quel Sovrano Protettore e fautore munificentissimo di ogni nobile studio, e d'ogni utile disciplina, che nella M. V. riconosciamo. » È questa munificenza che rese possibile la pubblicazione certamente onerosissima del grande trattato. Non posso dire di aver trovato documenti esaurienti; quello più diretto è un contratto, o forse soltanto un « compromesso », riguardante la stampa dei 4 volumi, il numero delle copie da stampare, il costo di ciascun foglio di stampa; questo contratto, che è su carta semplice, è conservato in un archivio privato della città di Biella ed è firmato soltanto da AMEDEO AVOGADRO da un lato e dal sig. BOGGIO Direttore (della Stamperia) dall'altro lato. Nessun cenno vi è di un eventuale intervento finanziario della Casa regnante. Forse non era quella la sede per far cenno all'intervento di Sua Maestà.

Nel discorso dell'on. FELICE CHIO, che successe ad AVOGADRO nell'insegnamento

Nel testo si riconosce subito una elevatezza non comune ad altri libri di fisica di quell'epoca italiani o stranieri. Vorremmo dire che è un trattato nobile, come nobile fu l'autore, un trattato che si limita ai capitoli che oggi diremmo della struttura della materia, sovente svolti sotto forma monografica. Non dobbiamo ignorare che, nel trattato, AVOGADRO introdusse un ampio capitolo sulla cristallografia, il quale segue strettamente le linee fissate dalle famose opere di R. J. HAÛY, C. F. NAUMANN, C. S. WEISS; e così questa scienza si rese accessibile agli italiani, nella loro lingua, e con alta malleveria.

Nel leggerne alcune pagine mi ha turbato un'idea, e chiedo ad altri di farne sicura esegesi; a me pare che in quelle pagine, scritte 120 anni or sono, risulti chiaro che per l'Autore « solido » si identificasse con « cristallo » (cioè sostanza cristallizzata); ancora una volta le idee di AVOGADRO precorrono i tempi di parecchi decenni.

Concluso il trattato di fisica, AVOGADRO ha avanti a sè ancor quasi un decennio di vita universitaria ed egli la dedica sostanzialmente al gruppo delle sue quattro memorie sui volumi atomici, di carattere decisamente chimico.

Il 21 Agosto 1850 trasmette alle autorità universitarie il « programma » pel suo insegnamento del prossimo anno; ma sul cadere del 1850 AVOGADRO, settantaquattrenne, rinuncia alla cattedra.

Per il suo ben meritato riposo? Non pare. *

Resta sulla barricata scientifica.

Da un lato continua per quattro anni ancora a scrivere i suoi appunti, nei suoi quaderni. Ormai scrive faticosamente, in un carattere spesso illeggibile, e le righe cascan giù verso la fine quasi che sentano anch'esse il peso degli anni. Ma AVOGADRO ha bisogno di prender nota di quel che avviene nella sua scienza.

Non sono più gli appunti pel suo futuro, come avvenne negli ultimi anni del secolo di prima, quando cominciò a riempire i quaderni di riassunti, di note, di estratti dai periodici scientifici più autorevoli dell'epoca e così da giurista si mutò in fisico e chimico, solitario autodidatta.

e che di lui fu intimo allievo — discorso per lo scoprimento al busto del Nostro nel cortile dell'Università di Torino (1857), — si legge esplicitamente « CARLO ALBERTO volle far sue le spese ingenti di quella pubblicazione ». Ma, invero, nello stesso discorso si legge: « a dimostrare l'importanza di questo principio [legge di AVOGADRO] basti dire che esso ebbe il patrocinio [*sic!*] del celebre AMPÈRE ». Ebbene mi si conceda di cercare ancora il patrocinio di qualche documento concreto per avallare definitivamente la munificenza reale. È anche da notare che nel suo *Trattato* AVOGADRO si firma in prima riga « Mastrouditore », in seconda riga « Professore Emerito » dell'Università. Infatti AVOGADRO era in quegli anni effettivo della prima carica e per essa retribuito circa il triplo che per l'altra; quest'ultima non doveva essere molto diversa da quella di un professore incaricato di oggi. Dalle norme universitarie di quell'epoca non sono riuscito a comprendere come mai AVOGADRO si dichiarasse « Emerito ».

Per sè solo egli scrive, per sè solo sembra sentire una massima: tu devi ancora sapere.

Dall'altro lato, il 22 Giugno 1851, già « a riposo » da un anno, egli legge all'Accademia delle Scienze di Torino la sua ultima memoria ⁽²⁸⁾ « sur les conséquences qu'on peut déduire des expériences de M. REGNAULT sur la loi de compressibilité des gas ».

Queste esperienze di REGNAULT ⁽²⁹⁾ fanno epoca nella fisica; fissano il diverso comportamento dei gas reali dai gas perfetti e tra di loro.

Nella fisica d'oggi nulla resta di quest'ultima memoria del Nostro.

Eppure essa va ricordata perchè io vedo in lei il testamento scientifico di AMEDEO AVOGADRO, conforme a quello che per cinquant'anni fu il suo programma di ricerca: dal groviglio dei fenomeni, dei valori numerici trai la legge; si direbbe che questa goda di restar nascosta e ardua impresa è il rintracciarla, ma è l'impresa degna dello spirito umano.

È la « fisica sublime », la scienza professata dal Nostro.

Così AVOGADRO settantacinquenne si cimenta, primo tra gli scienziati, alla equazione di stato dei gas reali.

Fu impresa fallita. Ma, dopo, quanti fallirono ancora e quali nomi! W. THOMSON e J. P. JOULE, J. C. MAXWELL, O. E. MEYER, R. CLAUSIUS, ...

Solo trenta anni dopo AVOGADRO, VAN DER WAALS (1881) vincerà.

Ricordiamo dunque con rispetto anche queste ultime pagine del Nostro.

* * *

Il 9 Luglio 1856 AMEDEO AVOGADRO si spegne.

Una tacita scomparsa, il rito solenne all'Università ove egli ha il saluto reverente di colleghi e discepoli, e la spoglia mortale abbandona Torino per la tomba di Quaregna.

* * *

Non ne è ancor asciutta la calce, e la teoria cinetica dei gas esplode.

Con data Luglio 1856, dunque tre settimane al più dopo la morte, AUGUSTO CARLO KRÖNIG, modesto professore in una Königliche Realschule di Berlino ⁽³⁰⁾ pubblica ⁽³¹⁾ in sette paginette i suoi *Grundzüge einer Theorie der Gase*.

⁽²⁸⁾ *Mém. R. Acc. Sc. Torino*, **13**, 171 (1853).

⁽²⁹⁾ *Ann. de Chim. et de Phys.*, **14**, 211 (1845).

⁽³⁰⁾ In un liceo, insomma.

⁽³¹⁾ *Pogg. Ann.*, **99**, 315 (1856); il fascicolo del periodico è del Settembre; la data del lavoro è « Luglio 1856 »; lo stesso lavoro dovrebbe essere stato pubblicato « poco prima » come opuscolo da A. W. HAYN, Berlino, ma non mi è riuscito saperne di più.

Su di un terreno ormai ben preparato per la teoria meccanica del calore, il breve lavoro di KRÖNIG fa l'effetto di una bomba.

« Per i gas », egli scrive, « farò una ipotesi che spiega subito le leggi di Mariotte e di Gay-Lussac [dell'eguale dilatabilità termica dei gas]; l'ipotesi è che le molecole siano equiparabili a sferette elastiche, in numero grandissimo nel volume considerato e ancor tuttavia così piccole da occuparne una frazione piccolissima ».

Invero KRÖNIG aggiunge subito la « proposta », e cioè l'ipotesi, che la forza viva media delle particelle possa assumersi a misura della temperatura assoluta del gas.

Insomma è, quasi alla lettera, la prima lezione elementare di teoria cinetica dei gas quale si svolge oggi.

KRÖNIG dimostra subito che nel suo gas cinetico, a parità di volume, pressione e temperatura, è contenuto lo stesso numero di molecole, qualunque ne sia la natura chimica.

KRÖNIG non dice che questa è la legge di Avogadro; non credo che lo sapesse.

Il lavoro di KRÖNIG fu presto sulla bocca di tutti, e curiose furono certe reazioni:

a) ma era quello che pensavo anche io, anzi sentite come sviluppo di più il concetto;

b) ma c'è già praticamente tutto in lavori di alcuni anni prima di J. P. JOULE;

c) già DANIELE BERNOULLI nella sua *Hydrodinamica* del 1738 aveva abbozzato proprio queste idee; furono ripubblicate le pagine di BERNOULLI.

Come si vede che, almeno nei casi eccezionali come questo, anche gli scienziati non sono tutti esenti dal sesto vizio capitale!

Bisogna riconoscere che molte cose dette dal KRÖNIG erano spuntate già fuori qua e là.

Ma è KRÖNIG a rivelare per primo che, dalla meccanica statistica nata col suo gas ipotetico, si deriva la ancor anonima legge di AVOGADRO.

Le pagine di KRÖNIG, limpide, lapidee, furono la favilla da cui divampò un vero incendio scientifico.

In pochi anni, per merito specialmente di CLAUSIUS e di MAXWELL, prende corpo la teoria cinetica dei gas; nasce poi la meccanica statistica classica.

E AVOGADRO?

Ora sta ai fisici non ignorarlo.

Per quanto mi consta occorre attendere il libro di O. E. MEYER ⁽³²⁾ perchè

(32) *Die kinetische Theorie der Gase*, 1^a ed., (Breslau, 1877).

nella teoria cinetica sia segnalato il nome di AVOGADRO accanto alla sua « regola ».

Ma intanto due fatti erano avvenuti.

Il primo fu il riconoscimento da parte del mondo chimico dell'importanza della legge di AVOGADRO fino allora o poco curata o addirittura ignorata; fu determinante per questo riconoscimento, presto divenuto universale, l'opera (1858) di un altro grande italiano, il chimico STANISLAO CANNIZZARO.

L'altro fatto è la prima determinazione sperimentale di quel fantomatico numero di molecole (integranti) che avrebbe dovuto essere lo stesso, per esempio, in 1 (cm)³ di un qualunque gas (perfetto) in condizioni normali.

Trattavasi certamente di un numero immenso, ma occorre giungere fino a J. LOSCHMIDT ⁽³³⁾ perchè in modo ancor rudimentale, ma già inaspettatamente approssimato, si ottenga dalla teoria cinetica dei gas la valutazione di quel numero: $\approx 10^{19}$ molecole al (cm)³ di gas in condizioni normali!

È un numero che sgomenta, ma ormai lo si può misurare. Non è più un articolo di fede che tal numero esista, e si può provar se sia lo stesso nei vari gas (perfetti).

Io credo che non poco abbia contribuito al freddissimo accoglimento dell'ipotesi di AVOGADRO il buio persistito per mezzo secolo sul valore di quel numero ipotetico ⁽³⁴⁾.

Con CANNIZZARO, LOSCHMIDT, O. E. MEYER si chiude il periodo eroico della ipotesi di AVOGADRO.

Siamo alla soglia del 1880 e da ogni parte converge il consenso; l'ipotesi, la regola divengono la « legge ».

La validità di essa nelle soluzioni diluite constatata da VAN'T HOFF (1887) spingono questo scienziato ad annunciarne l'estensione con parole ammirate.

La memoria di AVOGADRO del 1811 è ripubblicata (1889) nella raccolta dei *Klassiker der Wissenschaften* di OSTWALD.

La legge di Avogadro diviene imperativa perchè è teorema necessario della meccanica statistica classica, offerto prematuramente ai chimici per meravigliosa intuizione.

E l'autorità della legge cresce col tempo.

⁽³³⁾ *Ber. der Wiener Akad. d. Wiss.*, (2a), 52, 395 (1865).

⁽³⁴⁾ E credo che abbia fortemente e negativamente contato la forma spesso usata da AVOGADRO per enunciare la sua ipotesi, e cioè che nei gas in pari condizioni di temperatura e pressione le molecole sono « a egual distanza ». Come non essere allora indotti alla immagine di molecole ferme in una struttura rigida... ma gasosa? Non dimentichiamo, però, che al principio dell'Ottocento si parlava con serietà della nebbia sospesa nell'aria, perchè fatta da vescicolette di acqua piene di...; come tante minuscole mongolfiere piene di... sospese e ferme.

Nel 1903 ancora VAN'T HOFF scrive: « la chimica fisica attuale si basa essenzialmente sulle leggi della termodinamica e sulla legge di Avogadro ».

Nel 1907, in una conferenza sul progresso delle discipline chimiche nell'ultimo quarantennio, NERNST dice: « la più importante delle leggi molecolari teoriche che noi possediamo, la regola di Avogadro, appare legge naturale assolutamente esatta ».

Sicchè nel 1911 l'acre amarezza che traspare da ogni pagina del magistrale « Discorso storico-critico » su AVOGADRO scritto da ICILIO GUARESCHI ⁽³⁵⁾, doveva considerarsi superata dal riconoscimento ormai universale dei meriti del Nostro. Ma quell'amarezza e la polemica che trasse spesso con sè devono esser perdonate, tanto si comprende che quelle pagine furono dettate da un affetto e un rispetto sconfinati per lo scienziato insigne e misconosciuto in vita.

E poi, la polemica non era ancora del tutto inutile se proprio intorno allo stesso anno J. PERRIN, l'illustre chimico-fisico francese, intitolò una sua monografia famosa *Les preuves de la réalité moléculaire*, e tra le prove di realtà (che evidentemente a quella data l'autore riteneva ancora discutibile) egli ben a ragione considera come la più probante quella della coincidenza (entro gli errori sperimentali) del numero di molecole trovato qualunque sia il metodo, dei parecchi ormai conosciuti, con cui lo si determini.

Non quest'altro mezzo secolo ha attutito la risonanza già mondiale dell'opera del Nostro.

Oltre il numero di molecole al (cm)³ di gas perfetto in condizioni normali, il numero determinato da LOSCHMIDT e che gran parte degli scienziati giustamente chiama il « numero di Loschmidt », si considera anche il numero di molecole contenute in una mole (grammomolecola) di qualunque sostanza chimicamente definita ⁽³⁶⁾.

È questa una *costante universale*, una delle più importanti della chimica e della fisica, di valore ancora incerto $\pm \approx 10\%$ intorno al 1911; oggi, dopo il « colpo di stato » di J. A. BEARDEN (1931), se ne dà il valore nella cosiddetta « scala fisica » in:

$$(6,0250 \pm 0,0004) \cdot 10^{23} \frac{\text{molecole}}{\text{mole}} .$$

⁽³⁵⁾ *Opere scelte di Amedeo Avogadro*, pubblicate dalla R. Accademia delle Scienze di Torino (Torino, 1911), pp. I-CXL.

⁽³⁶⁾ Questo numero è ≈ 22415 volte quello di LOSCHMIDT, che è numero relativo ai soli gas perfetti in condizioni normali. Il valore proposto come attualmente più probabile al Congresso internazionale sulle costanti fondamentali della fisica, che in questi giorni si tiene a Torino, è:

$$(6,02486 \pm 0,00016) \cdot 10^{23} \frac{\text{molecole}}{\text{mole}} \quad (\text{scala fisica}) .$$

Il numero ignoto ad AVOGADRO e a tutti gli scienziati della sua età è ormai conosciuto con maggior approssimazione che la popolazione di una grande città a un certo istante!

Più AVOGADRO si allontana da noi negli anni, più si moltiplicano i segni d'onore che gli sono offerti da coloro che professano la sua scienza.

Accanto al numero di Loschmidt, si diffonde sempre più il termine di « numero o costante di Avogadro » per la costante universale su indicata.

Su proposta già antica (1911; 1922) del grande fisico olandese H. KAMERLING ONNES, si introducono in fisica lo « stato di Avogadro » e la « temperatura di Avogadro » ⁽³⁷⁾; sono termini sanciti anche nel *Physikalisches Wörterbuch* del WESTPHAL, libro universalmente noto.

L'Uomo, sempre più a noi lontano, mentre la sua opera è sempre più a noi vicina, l'Uomo che in vita non scrisse mai per rivendicare una sua priorità, perdoni ai contemporanei che lo trascurarono. Glorizzata sarebbe stata la sua se, osannato da quelli, fosse ignoto oggi ai nipoti.

Nel disconoscimento di prezioso ingegno, AMEDEO AVOGADRO sa quanti eccelsi spiriti abbia a compagni: DANIELE BERNOULLI per la teoria cinetica dei gas, come si è detto; CRISTIANO HUYGENS per la sua teoria ondulatoria della luce; HERMANN HELMHOLTZ per il suo principio di conservazione dell'energia; JAMES CLERK MAXWELL per la teoria elettromagnetica della luce; SVANTE ARRHENIUS la cui tesi di laurea sulla dissociazione elettrolitica fu approvata per commiserazione e venti anni dopo ebbe il Premio Nobel

Di ERNESTO RENAN sono le parole: « la gloria eterna è di aver posto la prima pietra ».

Ma lo spirito capace di ciò deve essere preparato ad essere ricompensato anche con l'incomprensione.

Di AVOGADRO, sommamente modesto, sommamente solo, sommamente puro nella sua scienza e nella sua famiglia, non ho trovato nessun detto che valesse a chiudere queste mie parole.

Si sa; è abusato rimprovero agli uomini di sola scienza quello di essere « aridi ».

⁽³⁷⁾ Lo « stato di AVOGADRO » è quello di un gas che obbedisca senza limitazioni all'equazione di stato di un gas perfetto; per tale stato vale esattamente la legge di AVOGADRO; un gas reale, via via che se ne riduca la massa specifica (volumica), cioè se ne aumenti la rarefazione, va assumendo con approssimazione sempre maggiore lo « stato di AVOGADRO ».

La « temperatura di AVOGADRO » è la temperatura di un termometro a gas quando quest'ultimo sia portato allo stato di AVOGADRO; essa coincide quindi con la temperatura termodinamica ed è la temperatura limite, data da un termometro a gas reale quando questo tenda allo stato di AVOGADRO; la temperatura di AVOGADRO è dunque l'unica temperatura effettivamente (se pur faticosissimamente) misurabile con un termometro a gas « perfetto ».

È soave poesia quella del poverello di Assisi: « Laudato si' mio Signore, per sor aqua la quale è multo utile et humile et pretiosa et casta ».

È ancor poesia il fantasticar dell'acqua elemento tra i quattro costituenti il nostro mondo.

È « arido », invece, CAVENDISH, che rivela l'acqua composta da idrogeno e ossigeno.

È ancor più « arida » nel tempio della Scienza la lapide perenne sulla quale è inciso:

acqua è H_2O

1811, AVOGADRO scrisse.

* * *

Nessun detto solenne, dicevo, ho trovato negli scritti di AVOGADRO ⁽³⁸⁾.

Ma che conta se tutta la sua vita è un tacito monito di come si deve operare per esser degni del rispetto del prossimo; e lo intende questo monito sol chi sia vergine di ogni ambizione?

Che conta allontanarsi ignoto dalla scena del mondo se oggi non vi è uomo colto sulla Terra che non ripeta il suo nome?

Che conta che il suo monumento nella sua città ⁽³⁹⁾ sia solo una modesta stele, modesta come Egli fu modesto, e sia posta in luogo solitario, come Egli fu solitario; ma è posta nel luogo certamente a lui più caro, all'ombra della sua casa spirituale ⁽⁴⁰⁾.

Che conta tutto ciò se possiamo dire con orgoglio che questa stele è l'unico monumento in Torino (e non solo in Torino) che sia stato eretto col contributo spontaneo di mille e mille e mille sottoscrittori di ogni classe e di dieci e dieci e dieci nazioni diverse, tutti uniti nel suo nome ⁽⁴¹⁾?

⁽³⁸⁾ E non ne conosco una conferenza, un discorso nei quali spigolare!

⁽³⁹⁾ Vi è anche il busto, eretto nel 1857, nel cortile d'onore dell'Università.

⁽⁴⁰⁾ La stele è nel giardino dell'Istituto di Fisica dell'Università.

⁽⁴¹⁾ Rintracciare i documenti per il mio scritto fu spesso, ma non sempre possibile.

Ringrazio quanti mi hanno aiutato: i Sindaci di Biella, Moncalieri, Quaregna, Torino; il prof. M. ALLARA, Rettore dell'Università di Torino e il Dott. STRUMIA della Segreteria Universitaria alacre ricercatore nei suoi archivi e anche fuori; il Dott. GARRETTI, Direttore dell'Archivio di Stato; il cav. PASTORE, Archivista del Municipio di Torino; il dott. MARUZZI, Bibliotecario della Accademia delle Scienze di Torino che mi fu prezioso nelle consultazioni della Biblioteca Accademica; il cav. BORRIONE, Bibliotecario della Civica di Biella; i colleghi DEAGLIO, MILONE, STILLE (Germania), TAPPI e l'ing. B. BERIA; i familiari dei rami collaterali agli AVOGADRO; e chiedo venia se altri mi sfugge.

Significato delle costanti fondamentali in Fisica.

R. DEAGLIO

Istituto di Fisica dell'Università - Torino

La scelta dell'argomento su cui dire brevi cose è caduta sulle costanti fondamentali, sulla loro importanza e sulla loro influenza nel progresso del pensiero scientifico. Di queste mi limiterò ad accennare a quelle di carattere universale.

Il mondo fisico, da quello a scala atomica a quello di scala astronomica, può essere sottoposto ad un tentativo di descrizione con l'uso di un ristretto numero di costanti indipendenti: esse compaiono nelle leggi fondamentali che sono alla base della fisica e con le quali la fisica teorica tenta di interpretare in un quadro unitario i vari fenomeni.

La storia delle costanti fisiche è la storia dello sviluppo dei concetti fisici. Essa potrebbe ben farsi iniziare dal giorno in cui nell'uomo, che si familiarizza con i più semplici fenomeni della natura, prende consistenza il criterio della misura.

Ufficialmente, almeno nei riguardi di ciò che sto per dire, la storia delle costanti fondamentali si può far nascere nel 1682 con la legge dell'attrazione universale di NEWTON, e non voglio con questo dimenticare o recare torto a RÖMER che nel 1676 per primo dava una risposta al quesito se la luce dovesse avere una velocità finita, e la risposta venne data con la sua celebre definizione della velocità stessa con metodo astronomico, ma solo più tardi, molto più tardi, la velocità della luce entra e domina le vicende della fisica teorica.

La costante che compare nella legge di gravitazione di NEWTON è una costante universale che stabilisce un legame unico fra la massa inerziale e la massa gravitazionale, fra la meccanica dei corpi e la meccanica celeste. Dovrà passare più di un secolo prima che si istituisca l'esperienza capace di dare il valore della costante gravitazionale; risale a CAVENDISH nel 1798 la celebre misura con la bilancia di torsione e la legge di NEWTON nel secolo XIX diventerà fondamentale per la meccanica classica.

La determinazione della costante universale di gravitazione della legge

di NEWTON è la prima tappa sulla strada della conoscenza del mondo fisico, è il primo risultato di un metodo d'indagine non soltanto speculativo ma sperimentale alla cui origine troviamo GALILEO.

Seguire questo metodo significa per il fisico ricondurre lo studio di un fenomeno, qualunque esso sia, allo studio di una serie di problemi più semplici, per ognuno dei quali si hanno sufficienti informazioni per la soluzione. Ognuno di questi problemi ha la sua incognita e trovarne la soluzione significa determinare con sufficiente precisione e certezza il suo valore, al quale si conferisce il nome di costante.

Ogni nuova costante significa quindi l'eliminazione di una delle numerose incognite nell'interpretazione dei fenomeni naturali ed un passo ulteriore nel cammino della conoscenza che è lo scopo ultimo della ricerca.

Fra tutte le soluzioni dei problemi che il fisico si pone seguendo tale metodo di indagine, ve ne saranno di quelle indipendenti tra di loro, ed è più propriamente a queste soluzioni indipendenti che spetterà la specificazione di costanti fondamentali.

Sono note le conseguenze della meccanica newtoniana alla quale è associata la costante di gravitazione. L'opera di NEWTON spalanca la porta al mirabile successivo sviluppo della meccanica per opera di EULERO, D'ALEMBERT, LAGRANGE, LAPLACE, HAMILTON e JACOBI.

È anche noto come la fisica in quel periodo si identificasse prevalentemente con la meccanica anche se in taluni casi, come nella dinamica dei fluidi e dei gas si rendesse indispensabile l'aggiunta di concetti termodinamici.

Più tardi, nella fisica si sviluppa l'elettromagnetismo, indipendentemente dalla meccanica anche se taluni concetti fondamentali sono da questa derivati, come il concetto di carica da quello di massa, la legge di COULOMB dalla legge di NEWTON ed i concetti del campo elettrico e magnetico della teoria della gravitazione.

Dopo un secolo di ricerche in questo campo la sintesi dell'elettromagnetismo compendiata nelle celebri quattro equazioni di MAXWELL istituisce una nuova costante, il rapporto tra l'unità di carica elettrostatica e l'unità di carica elettromagnetica, rapporto che, determinato cent'anni fa precisi da WEBER e KOHLRAUSCH, si identifica con la velocità della luce. Tale costante, la velocità della luce, è caratteristica di tutte le teorie dei campi.

È pure del secolo XIX il grande movimento dal quale prende origine lo sviluppo della chimica su basi scientifiche.

Il moderno concetto di atomo e di molecola era stato inventato dai chimici per giustificare le leggi quantitative della chimica, le leggi delle proporzioni costanti e delle proporzioni multiple; ma solo nel 1811 AVOGADRO a conclusione dei suoi studi sulla teoria molecolare procede alla formulazione della sua ipotesi che in seguito assurgerà al valore di legge: il numero di molecole per grammomolecola è una costante.

Sono noti gli sviluppi della chimica a partire da questa legge che il CANNIZZARO nel 1858 impose all'attenzione degli scienziati. Sviluppi a cui sono associati i nomi di BERZELIUS, PROUT, CANNIZZARO, DUMAS, FARADAY.

Si dovrà arrivare fino al 1865 perchè il numero di Avogadro prenda la fisionomia concreta del suo valore attpverso il computo LOSCHMIDT del numero di molecole contenute in 1 cm^3 di aria in condizioni normali. Tale è l'importanza del valore del numero, N , di AVOGADRO che la sua precisa determinazione sarà oggetto di ricerche attraverso fenomeni fisici di natura assai differente; dal metodo delle sospensioni colloidali di PERRIN all'irraggiamento del corpo nero.

Si ha in questo campo un primo grandioso complesso di misura di costanti (la misura dei pesi atomici degli elementi), ed il primo esempio dell'importanza che può trarre il pensiero scientifico dalla precisa loro valutazione.

Il MAYER già nel 1869 intravede che la natura degli elementi chimici è funzione del loro peso atomico, ed il MENDELEJEV alla stessa epoca, constatata la periodicità delle proprietà fisiche e chimiche degli elementi chimici in funzione del peso atomico, stabilisce la prima tabella del sistema periodico, tabella che trova la sua definitiva forma nel 1914 per merito di MOSELEY.

Lo sviluppo della ricerca chimica e delle teorie fisico-chimiche prende lo spunto da alcune correlazioni che scaturiscono dalla conoscenza dei pesi atomici degli elementi e pone termine al periodo grigio dominato dall'empirismo alchimistico.

Prende vita ed ardore quel progresso nel campo della chimica e della chimica-fisica per arrivare attraverso la scoperta degli isotopi, alla teoria elettronica della valenza, alla chimica delle strutture, all'attuale chimica nucleare.

Ad altri il compito di collocare nella sua giusta posizione la legge di AVOGADRO e la parte che essa ha nello sviluppo della scienza.

È anche di questi tempi, del 1850, che l'atomistica fisica prende sviluppo per compendiarsi nella teoria cinetica dei gas che ancora fa uso di schemi e leggi della meccanica newtoniana, ma colla teoria cinetica dei gas entra nella fisica un nuovo criterio per lo studio dei suoi complessi problemi, il criterio di probabilità legato a grandezze fisiche medie relative a sistemi di moltissime particelle.

Con questo criterio acquista ruolo di fondamentale importanza il celebre principio di BOLTZMANN (siamo nel 1887) che stabilisce un legame fra le grandezze meccaniche e termiche; voglio dire la loro proporzionalità fra entropia e probabilità di un sistema, e si introduce una nuova costante fondamentale, k , nota come costante di BOLTZMANN. Si può ben dire che la teoria cinetica dei gas è la teoria della costante k .

Indipendentemente dalla teoria cinetica matura una atomistica per l'elettricità che prende lo spunto dalle leggi enunciate da FARADAY nel 1834. Nel 1891 STONEY designa col nome di «elettrone» la più piccola carica negativa, l'atomo

di elettricità. Tutti i fatti sperimentali confermano in seguito che tutte le cariche elettriche sono sempre multipli interi positivi o negativi di questo atomo di elettricità, arriviamo così nel 1897 da parte di THOMSON e VICKERT alla scoperta effettiva dell'elettrone. L'importanza che assumerà questa particella che è uno dei costituenti stabili degli atomi, nel progresso della fisica, giustifica i numerosi dispositivi che il fisico ha allestito per misurare con approssimazione enorme (1:500 000) il valore della sua carica ed il valore della sua massa a riposo.

E si comprende quale importanza abbia la conoscenza della carica dell'elettrone se si pensa al suo stretto legame col numero di AVOGADRO e colla costante di BOLTZMANN.

Nel 1900 PLANCK intraprende il calcolo della ripartizione spettrale dell'energia per un sistema composto di un gran numero di risonatori; questo calcolo conduce effettivamente ad un'espressione dell'entropia dalla quale si deduce la distribuzione spettrale dell'irraggiamento di un corpo nero, alla condizione di ammettere in manifesta deroga con le idee classiche, un'atomicità dell'energia emessa da un risonatore di frequenza ν : energia che necessariamente deve essere un multiplo di un quanto $\varepsilon = h\nu$. La costante h detta costante di PLANCK è una costante universale che ha le dimensioni di un'azione.

L'introduzione di questa costante rappresenta qualcosa di assolutamente nuovo, essa è destinata a demolire un pensiero fisico fondato sul concetto di continuità, inerente a relazioni casuali.

Il valore di h è ritrovato successivamente da LENARD, POHL e PRINGSHEIM, MILLIKAN ed altri. Ricordo ancora le belle esperienze di FRANK e HERTZ sulla perdita di energia negli urti elettroni-atomi, dove la costante h si deduce dalla determinazione della velocità critica che un elettrone deve possedere per provocare l'emissione di un quanto di luce.

D'altra parte nel 1905 la teoria della relatività ristretta, nata dalla difficoltà dell'ottica dei corpi in moto, postula la costanza della velocità della luce che raggiunge il valore limite c nel vuoto: c è una costante universale, essa conferisce un valore euristico al principio di relatività formulato da EINSTEIN: «tutte le leggi della natura sono covarianti per la trasformazione di LORENTZ».

Il magistrale sviluppo delle teorie fisiche è legato a queste costanti: con le costanti c ed e si costruisce l'elettrodinamica classica, con la costante c la relatività ristretta, con la costante h la meccanica ondulatoria quantica.

Il postulato della costanza della velocità della luce segna nella storia della fisica il definitivo abbandono dei concetti astratti ai quali la mente del fisico si era ancorata; in particolare al concetto di etere, così caro a FRESNEL, che già l'opera di MAXWELL aveva relegato al ruolo di sistema di riferimento.

L'incapacità della elettrodinamica classica nello studio del comportamento dei sistemi alla scala atomica, ha condotto il BOHR all'introduzione della costante h nella sua celebre teoria che nel 1913 segna la nascita della meccanica quan-

tistica. Alla teoria di Bohr è volta l'attenzione generale dei fisici, ed il suo sviluppo diventa rapidamente un'opera collettiva. Le cinque ipotesi enunciate da BOHR di cui la terza più impegnativa riguardante l'irraggiamento emesso dal sistema atomico quando esso passa da una configurazione ad un'altra entrambe stazionarie, portano nella teoria di Bohr alla giustificazione della serie di BALMER, ed al significato fisico della costante di RYDBERG il cui valore viene a dipendere da h . Le determinazioni della costanti di RYDBERG fatte da PASCHEN sulle linee dell'idrogeno e dell'elio costituiscono una decisiva verifica del modello atomico di BOHR.

Col 1913 si inizia con maggiore consapevolezza un fecondo sviluppo nel campo della conoscenza. I fisici incominciano allora quella profonda evoluzione delle teorie fisiche quantizzando e rendendo relativistiche le loro equazioni. D'altra parte lo sviluppo della fisica teorica faceva convergere l'attenzione sulla necessità di una sintesi fra i concetti di onda e di particella.

Mentre la presenza di numeri interi nelle relazioni quantiche faceva pensare ad una analogia formale colle classiche relazioni di interferenza della teoria ondulatoria, l'analogia del principio della minima azione chiave di volta della meccanica classica, col principio di Fermat chiave di volta dell'ottica geometrica, suggeriva che la meccanica classica potesse essere una forma approssimativa di una meccanica ondulatoria più generale, come l'ottica geometrica rispetto all'ottica fisica.

Nasce così nel 1923 la meccanica ondulatoria la quale, dominata dalla costante h , darà successivamente luogo alla moderna meccanica ondulatoria relativistica ed all'elettrodinamica quantistica, dove oltre alla costante h , compaiono le costanti c ed e .

Appare da questi brevi e schematici accenni dello sviluppo del pensiero scientifico nella fisica da NEWTON ad oggi, la parte fondamentale che ha un gruppo di costanti N , e , h , c di carattere universale che inquadrano in teorie coerenti un mondo fisico congeniale alla nostra abitudine mentale, un mondo fisico, la cui conoscenza è limitata, oserei dire, dalla degradazione di un messaggio emesso in messaggio osservato.

Di tutte le costanti fondamentali che il fisico usa in modo appropriato nello studio dei fenomeni della natura, siano essi in scala atomica od in scala astronomica, costanti sulle quali mi sono ora dilungato, due di esse, la costante h di Planck, e la velocità c della luce nel vuoto, maggiormente si pongono in rilievo nel progresso della fisica teorica. Su di esse, come si è detto, si fonda la meccanica quantistica, la meccanica ondulatoria relativistica, l'elettrodinamica quantica, che colla teoria della relatività costituiscono oggi il quadro più completo della nostra attuale interpretazione del mondo fisico.

Nelle varie teorie compaiono pure e con carattere di universalità le masse di riposo m_N e m_e , dei nucleoni dell'elettrone, che sono le particelle elementari sensibili costituenti qualsiasi atomo.

Il valore di tutte queste costanti è stato oggetto di lunghe ricerche sperimentali, ed avremo occasione di sentire in questo congresso quali spettacolose approssimazioni si sono raggiunte nella loro determinazione. Queste costanti sono dimensionali, il loro valore numerico dipende dalla scelta delle unità di misura che, come voi sapete, è quanto mai convenzionale.

Si comprende allora il criterio che in un secondo tempo ha spinto alla ricerca di opportune combinazioni di costanti universali tali da ricavare dei semplici coefficienti numerici adimensionali detti, forse impropriamente, *costanti pure*.

Una di queste è la costante $e^2/\hbar c = 1/137$, rapporto fra l'azione associata alle particelle e l'azione associata alla radiazione. È nota l'importanza di tale costante, detta costante di struttura fine, nella spettroscopia e nell'elettrodinamica.

Altri coefficienti numerici sono il rapporto fra le masse del protone e dell'elettrone $m_p/m_e = 1836$; il rapporto fra l'attrazione elettrostatica e l'attrazione gravitazionale che si esercita fra protone ed elettrone $e^2/\gamma m_p M_e = 2,28 \cdot 10^{39}$.

Non si può passare sotto silenzio lo sviluppo della teorie cosmogoniche alle quali hanno contribuito menti elette. Anche in questo campo noi ritroviamo delle costanti sulle quali fanno perno le varie ipotesi sulla creazione e sul divenire dell'Universo. Per far vedere come si arrivi anche qui a delle costanti, ricordo la teoria di Hubble che viene derivata dall'applicazione della teoria dell'effetto Doppler per l'interpretazione nello spettro delle galassie della recessione di linee spettrali note di elementi verso il rosso: recessione tanto più grande quanto maggiore è la distanza della galassia: è la teoria dell'Universo in espansione. La costante di proporzionalità che compare nella teoria di Hubble, è appunto la costante di HUBBLE, e rappresenta la velocità di recessione di una galassia per unità di distanza (il valore della costante di HUBBLE è $545 \text{ km sec}^{-1} \text{ megaparsec}^{-1}$). Il reciproco della costante di Hubble, $T = 1,8 \cdot 10^9$ anni è una grandezza molto importante: essa rappresenta l'età dell'universo.

Orbene appare molto interessante che l'età di diverse parti della nostra Galassia desunte attraverso metodi completamente differenti, concordi come ordine di grandezza (qualche miliardo di anni) con quello definitivo della costante di HUBBLE ossia con l'ipotesi dell'espansione dell'Universo: ipotesi che d'accordo coi risultati sperimentali dovrà essere qualche po' modificata; e badate che la definizione di una costante implica la definizione di vari metodi sperimentali atti alla misura del suo valore. Ricorderò a proposito che l'età della terra si può dedurre con buona sicurezza dal decadimento di diversi elementi radioattivi e dalla loro abbondanza relativa sul nostro pianeta. Le misure più recenti in questo senso concordano nel valutare l'età della terra in circa 2 miliardi di anni.

Le costanti fondamentali su cui mi sono particolarmente soffermato, ed altre a cui ho accennato stanno ad indicare le grandi acquisizioni del progresso scientifico. C'è da pensare che con esse il fisico possa procedere ancora oltre i limiti oggi raggiunti. Ma certo è che a questo punto conviene meditare sulla vastità di quanto ancora ignoriamo, ed a ciò che potrà essere una più vasta sintesi della scienza futura.

Per il fisico oggi la questione non è tanto di sapere se esso deve assiomatizzare la fisica, in quanto forse la forma assiomatica è la forma più utilizzabile della sua conoscenza, ma di fare evolvere gli assiomi, i suoi assiomi, ed il suo metodo di deduzione, dalle crescenti informazioni che la natura gli comunica attraverso la magistrale tecnica sperimentale che il suo genio ha messo in movimento.

Words spoken in Memory of Amedeo Avogadro and for the Opening of the Congresses.

R. T. BIRGE

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In un mondo pieno di aspirazioni e gelosie nazionali una, conferenza scientifica internazionale è una impresa molto desiderabile. Credo che tra tutti i campi di attività intellettuale, comprese l'arte, la musica e la letteratura, non c'è campo che mostri un grado più grande di cooperazione internazionale che quello delle scienze e specialmente quello delle scienze fisiche.

I fenomeni della Natura hanno un valore universale, e chiunque li può studiare e verificare sperimentalmente senza riguardo a razza o nazionalità: per questa ragione non ci possono essere differenze fondamentali di opinione riguardo a questo tipo di conoscenza. Gli scienziati sono però degli esseri umani e per il progresso della scoperta scientifica è di enorme importanza, per quelli che sono coinvolti in questo compito comune, di conoscersi personalmente tra di loro.

Proprio per questa ragione sono del parere che una conferenza di questo genere sia del massimo valore non solo per aumentare le conoscenze personali ma anche per fomentare la capacità di intesa reciproca tra le nazioni. Soltanto attraverso un'intesa reale e a una reciproca confidenza possiamo sperare di arrivare ad una vera pace nel mondo.

E così a nome di tutti gli scienziati convenuti, desidero esprimere i nostri profondi e sinceri ringraziamenti alla città di Torino per tutti i suoi preparativi e sforzi sia finanziari sia di altra natura compiuti per offrire questo Congresso Internazionale sulle costanti fondamentali della fisica. E voglio ringraziare tutti gli organizzatori, in modo particolare i proff. POLVANI e DEAGLIO che hanno contribuito con tanto successo a che questo Congresso, risulti degno dell'illustre fisico italiano, AMEDEO AVOGADRO, nel cui nome e a onore del quale ci siamo qui riuniti.

* * *

The correctness of the foregoing Italian words I owe to my dear colleague, Professor EMILIO SEGRÈ. The doubtless bad pronunciation I owe entirely to myself. It is my first attempt to speak in Italian, a language I have never studied. In fact, I presume that the greatest factor in continuing the misunderstandings between nations is just this condition of diversity of language.

For that reason a truly universal language is something greatly to be desired, although all attempts thus far to introduce an artificial universal language have gained little support. Apparently the nearest approach we now have to a universal language is just the English language itself. This fact is recognized in the present gathering, where nearly all of the papers will be delivered in English.

An editorial in *Nature*, of November 19, 1955, states that at present 50 percent of all scientific papers are written in English, 15 percent in French, 15 percent in German, and 10 percent in Russian, leaving only 10 percent for all other languages, including Italian and Spanish. But if the *Nuovo Cimento* continues its present near monopoly of papers on meson physics, I think that the Italian percentage is certain to rise.

AMEDEO AVOGADRO was born in Torino on August 9, 1776 and died here on July 9, 1856. He was a member of a distinguished Italian family, and in accordance with the vocation of the family, he became a bachelor of law and later doctor of ecclesiastical law. After practising for a time he became interested in mathematics and physics, and in 1809 he was appointed professor of physics in the Royal College of Vercelli. In 1820 he was appointed to the newly created chair of mathematical physics, in Torino, and continued in that position until his retirement in 1850, except for a decade during which the chair was abolished for political reasons. The 4-volume, *Trattato*, printed for private distribution by the Torino Academy of Sciences in 1911, contains more than 50 of his publications, of which only his famous paper of 1811 is generally known.

The history of the Atomic-Molecular Theory, to which AVOGADRO made such a major contribution, is discussed in detail in one of the excellent Harvard Case Histories, with that title ⁽¹⁾. During the period 1800-1803 JOHN DALTON gave the first clear formulation of an atomic theory, although the first printed account of his work appeared in a book by THOMAS THOMSON, published in 1807. The work of GAY-LUSSAC, on the law of combining volumes, first announced in 1808, formed the experimental basis for AVOGADRO's hypothesis,

⁽¹⁾ L. K. NASH: *The Atomic-Molecular Theory*, Harvard Case Histories in Experimental Science. Case 4 (1950), pp. 115.

announced three years later by him in a paper of fundamental importance, published in the French *Journal de Physique* (2).

AVOGADRO did not like the word «atom», used by DALTON and others, and he introduced, instead, the word «molecule», which means «small mass». He then used various modifying adjectives. Thus he employed «elementary molecule» for our «atom», «integral molecule» or «compound molecule» for the molecule of a compound, like NaCl, and «constituent molecule» for the molecule of an element, like N₂. He was the first person to suggest that two identical atoms could unite to form a molecule, an assumption that was necessary in order to explain some of the results of Gay-Lussac on combining volumes.

I give only two brief extracts from AVOGADRO's 1811 paper, quoting directly from the Harvard Case History. The first reads as follows (3):

«M. GAY-LUSSAC has shown in an interesting Memoir that gases always unite in a very simple proportion by volume, and that when the result of the union is a gas, its volume also is very simply related to those of its components. But the proportions by weight of substances in compounds seem only to depend on the relative number of molecules which combine, and on the number of compound molecules which result. It must then be admitted that very simple relations also exist between the volume of gaseous substances and the numbers of simple or compound molecules which form them. The first hypothesis to present itself in this connection, and apparently even the only admissible one, is the supposition that the number of integral molecules in any gas is always the same for equal volumes, or always proportional to the volumes.»

Here then we have the original statement of Avogadro's hypothesis. Later in the paper, after giving the mass of the atom (his molecule) of oxygen in terms of that of hydrogen, on the basis of this hypothesis, he goes on to say (4):

«On the other hand, since we know that the ratio of the volumes of hydrogen and oxygen in the formation of water is 2 to 1, it follows that water results from the union of each molecule of oxygen with two molecules of hydrogen.»

He then gives, by similar reasoning, the correct molecular constitution of ammonia, nitrous oxide, nitric acid, etc.

In spite of this very clear and correct statement, water was usually denoted

(2) AMEDEO AVOGADRO: «Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps, et les proportions selon lesquelles elles entrent dans ces combinaisons», in *Journ. de Phys.*, 73, 58 (1811).

(3) Reference (1), p. 72.

(4) Reference (1), p. 76.

as HO, instead of as H_2O , up to the middle of the nineteenth century, and the Avogadro hypothesis was not generally accepted until several years after his death. The reasons for this failure to recognize the truth or importance of his work form a long story. One of the main objections to his theory resulted from a belief that it was absurd to assume that two *identical* atoms could unit to form a molecule. The fact that a gas resisted compression was supposed to prove that *like* atoms *repelled* each other and therefore could not possibly exhibit the strong attraction shown by the *unlike* atoms of an ordinary molecule like NaCl.

The eventual acceptance of the Avogadro hypothesis came primarily as a result of the work of another Italian physicist, STANISLAO CANNIZZARO, born in Palermo and Professor in Genoa, as given in his «Saggio di un Corso di Filosofia Chimica», published in the *Nuovo Cimento*, 1858, or nearly half a century after Avogadro's original paper.

In this very brief talk there is not time to enter into further details of a most interesting episode in the history of physical science.

PARTE SECONDA

Rendiconti del Congresso Internazionale sulle Costanti Fondamentali della Fisica.

SEZIONE PRIMA: Questioni generali e sperimentali.

A Survey of the Systematic Evaluation of the Universal Physical Constants.

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1. - Introduction.

Science may be defined as the objective and systematic study of Nature. But such study is conducted by human beings, with all the frailties of human beings. As a result one often hears or makes remarks such as, « That is not a very scientific procedure », or « That is not a very scientific attitude ». In my work on the general physical constants I have, usually quite unexpectedly, come across many such situations.

Now to me the study of science is, in a sense, a religion. For there can scarcely be anything more marvelous than the structure of Nature, nor anything more satisfying than to aid, even in the smallest way, in the gradual unfolding of the intricacies of the structure of our universe. From the beginnings of the human race man has speculated on the wonders of his environment, but there is and can be nothing in even his wildest speculations in any way comparable to the actual facts of Nature. For just this reason the true objective study of science offers a never ending and wholly satisfying human endeavor, at least I have found it so.

This may well be the last paper I will ever write on the subject of the general physical constants. For that reason I should like to take the opportunity to consider briefly some aspects of the human side of this subject, as well as the colder and purely factual side. For if I have, to any degree, succeeded in calling attention to the numerous pitfalls that menace every research worker in science, and that lead so often to false results and conclusions, I consider that to be a far more valuable accomplishment than any specific scientific advance.

If, then, I make definite and personal references to many surprising and often unfortunate episodes, this is not done in any spirit of censure, but rather in the hope that future work may be more free of such blemishes. Furthermore, I have always felt that admonitions in general terms are quite meaningless and ineffectual. They must be formulated in terms of specific incidences.

The present paper will cover only a small portion of the work on any one constant and on only a few selected constants. A full account would require an address several days in length, instead of a mere hour or so. In the case of my last general paper [1] in this field, printed in 1941, I was asked by the editor to submit a 20-page paper. The final printed paper was, however, 44 pages in length and the title quite properly read, «The General Physical Constants as of August 1941, with Details on the Velocity of Light only». If I had gone into equal detail in the case of the other general constants the paper would have been several hundred pages long.

One of the most debatable subjects is the role of authority in science. Prior to the historic investigations of GALILEO, here in Italy, most if not all accepted truth in the field of science, as well as in other fields such as religion, was based on the pronouncements of some so-called authority; e.g. «Aristotle says that such-and-such is true. Therefore it must be true». That was, unfortunately, somewhat the situation in which I found the universal constants, when I quite unexpectedly and unintentionally became involved in the field.

A distinguished scientist would obtain a value of some such constant, which he believed more accurate than any previously found. He would make such a claim, in a published paper, and thereafter, for some longer or shorter period, his value would be generally accepted and used throughout the scientific world. A good example of this situation was Millikan's oil-drop value of the electronic charge, e .

In that case there was only the one exhaustive investigation. Another situation tended to develop when research workers residing in two or more countries were involved. Then the value of a certain physical constant often had a peculiar national flavor. If, for instance, a distinguished German scientist obtained one value, and a distinguished French scientist another value of the same constant, one usually found the German value used subsequently in German papers and texts, and the French value in French papers and texts. I am speaking here particularly of the situation fifty or more years ago. Fortunately international scientific relations are now far better.

Another unfortunate aspect of the situation, as I found it, was that the generally adopted value of each constant was chosen quite independently of the value of other, often related constants, so that no *consistent* set of values of the general constants existed. Thus, for instance, although everyone may have accepted the correctness of Bohr's formula for the Rydberg constant,

a formula that involves the values of the Planck constant and the charge and mass of the electron, no real attempt was made to adopt values of these three constants that were consistent with the known, highly precise spectroscopic value of the Rydberg constant. Even in more recent years this very illogical procedure has occasionally appeared in the literature.

A third, and quite annoying blemish in published and accepted values was the use, in their evaluation, of a variety of values of the various auxiliary constants that were involved in the calculation. There have even been instances of two *different* values of an auxiliary constant (the velocity of light) used in the *same* equation, as I shall illustrate presently. It is obvious that values of a fundamental constant, obtained by two or more different investigators, are not directly comparable unless the same values of the auxiliary constants are used in all cases.

A fourth, and related error has been the occasional failure to reduce the several measured quantities appearing in a certain formula to a common physical condition. For instance, in the evaluation of the Avogadro number from the measured properties of a given crystal, including its density and its grating space (i.e., unit cell spacing), one obviously should use values of both the density and the grating space for a common specified temperature. If, as is normally the case, these two quantities have been measured at quite different temperatures, then at least one of them must be reduced by the use of a thermal coefficient. But in some of the earlier work I actually found data for two different temperatures thus used, with no reduction to a common temperature.

When such a reduction *is* made, the thermal coefficient thus used constitutes an «auxiliary» constant, and in the case of crystals, there is in general a relatively large uncertainty in its measured value. An additional, and quite common error, especially in earlier days, has been the failure to make any allowance for the uncertainty in such an auxiliary constant, in estimating the uncertainty of the final result.

A fifth defect is the occasional use of an approximate formula, with no indication of the magnitude of the error thus introduced. Often one sees a statement to the effect that a certain correcting quantity is «negligibly small» and hence has been neglected, but with no indication of the actual magnitude. What should always be done is to state this magnitude and then leave it to the reader to judge whether or not it is negligible. All too often a certain correcting quantity is in fact negligible in the work in question, but then it continues to be neglected in later and far more precise work when it has become not at all negligible. This situation arises just because subsequent workers have not realized the actual magnitude of the correction, and have failed to evaluate it themselves. Examples of such errors will be given later.

An even more serious related defect is the failure to state explicitly just what formula has been used to calculate a certain quantity, so that the reader

cannot tell whether an exact or an approximate expression has been employed. This failure to include in a published paper sufficient information to show how a certain numerical magnitude has been calculated applies also to other of the defects already noted. Thus it was all too common practice, twenty or more years ago, to neglect to state the value that had been adopted for one or more of the auxiliary constants involved. For just this reason it was often quite impossible for me to reduce many printed results to truly comparable values, although some additional information along this line was acquired by means of extensive private correspondence, mainly with American workers.

In addition to this failure to give sufficient information regarding details of the calculation, investigators very frequently have made no real attempt to estimate the uncertainty involved in each phase of the work; and even when a final uncertainty was published, it was sometimes unclear whether the uncertainty was intended to represent a probable error, a standard deviation (the German « mean error »), or a so-called « maximum uncertainty » or « limit of error » (expressions, incidentally, that are quite devoid of scientific meaning, as will be discussed later).

The final, and possibly most serious defect of all has resulted, in many investigations, from the use of purely *ad hoc* and ill-advised methods of calculation. This is a subject on which I could easily speak at great length. When you have heard the paper by Dr. COHEN you will realize better the really enormous improvement in the situation that exists at the present time.

When I started my work on the calculation of the general constants, the method of least squares was in common use by surveyors and by astronomers. But it was seldom used by anyone else. In fact, a great majority of the physicists and chemists, including some of the most distinguished investigators in these fields, were not sufficiently acquainted with the technical details of this method of computation to use it intelligently, even if they had desired to do so.

In the introductory paragraph of my 1929 paper on the general constants [2], I made a plea for the use of the method of least squares. I even included the very simple formulas for the least squares values of the two coefficients of a linear equation, and for the probable errors of the values thus calculated. In 1932 I gave a much more extended discussion [3], with special emphasis on the method of calculating least squares probable errors on the basis of internal consistency and external consistency (names, but *not* methods, that I invented at that time). These methods were applied to available data on the atomic constants in an immediately following paper [4], but the situation at that time was rather confused and no change was recommended for the 1929 values.

The objection to the use of least squares on the part of many scientists

has always seemed to me very strange. Thus the final evaluation of any measured constant *necessarily* involves a certain amount of calculation – sometimes fairly involved calculation. Consequently everyone is forced to adopt *some* method of calculation, and when a purely *ad hoc* method is adopted, the investigator should be under some obligation to show that his special method is superior to that of least squares, or of some other carefully formulated procedure. But such a defence is never made, and in fact seldom could be made. The method of least squares, like any other scientific method, must be used with discretion and with a little common sense. But when it is so used, it is certainly superior to any other proposed method in the overwhelming majority of all experimental work in the field of physics.

One of the few eminent physicists who has published his experimental results in sufficient detail to make extensive recalculations possible is the late R. A. MILLIKAN. This statement is particularly true in respect to his oil-drop value of the electronic charge. Also, as it happens, that work aptly illustrates several of the defects that have just been noted. Hence it furnishes a convenient example of the more or less incorrect and misleading results that follow from the use of certain questionable procedures.

2. – Value of the electronic charge.

The universal acceptance of MILLIKAN's [5] final oil-drop value of e , $(4.774 \pm 0.005) \cdot 10^{-10}$ esu, from 1917 until about 1930 is a good example of complete reliance on authority. Not only was his result accepted without question by everyone, but no one else even attempted similar work of comparable precision. I was apparently the first person to question his actual result, and then not in criticism of any of the observational work, but purely on the basis of his adopted values of certain auxiliary constants, and of the method of calculation used in obtaining the final result.

It should be noted, at this point, that the uncertainty, ± 0.005 (or 0.1 per cent), published by MILLIKAN was not intended by him to represent a probable error, or a standard deviation. He announced it as the *maximum uncertainty* in his result. But the DUMOND and COHEN present best value of e is $(4.80286 \pm 0.00009) \cdot 10^{-10}$ esu (or 0.002 percent). Thus Millikan's result was actually in error by nearly *six* times his announced maximum uncertainty.

Doubts concerning his value of e had begun to arise while I was working on my 1929 paper. They came as a consequence of an entirely new method of evaluating e , one using crystal and X-ray data, combined with the value of the faraday, F . The new method leads directly to a value of the Avogadro number, N , and will be discussed in some detail later in this paper. Then we have $e = F/N$. Within a few years it became evident that the new method

led to a much more reliable value of e than did the oil-drop method, and that Millikan's value was seriously in error.

This discovery stimulated not only new work by other investigators on the oil-drop method, but also—and more importantly—a number of new determinations of the viscosity of air. The results of all such work, carried out mainly between 1936 and 1939, were critically examined in my 1945 paper on certain atomic constants [6]. The weighted average of six new determinations of the viscosity, three by the rotating cylinder method and three by the capillary tube method, is $(1832.45 \pm 0.69) \cdot 10^{-7}$ c.g.s. units, as contrasted with the 1822.6 value used by MILLIKAN.

When this new value is combined with the oil-drop data found in four different investigations, including that of MILLIKAN, the final weighted average of e is 4.8130 ± 0.0064 , a value larger than the DUMOND and COHEN present best value by 0.21 percent, or 1.6 times the calculated probable error. But MILLIKAN's own result of 4.8071 ± 0.0038 (with the use of the new viscosity value) is only 0.087 percent too high, or only 1.1 times the probable error of his work. Moreover, it should be noticed that this probable error, and those that I have assigned to the work of other investigators, are based *only* on the statistical fluctuations of the plotted data, with no allowance for systematic errors of any kind.

The corresponding values of e for the other three investigations [7], as given in G.C. 1945 [6], are respectively 0.22 percent too high, 0.25 percent too low, and 0.88 percent too high, on the basis of the latest value. Thus Millikan's own oil-drop work leads to a far more correct value of e than that of any of the later oil-drop investigations, and the error in his published value resulted almost entirely from his use of a very incorrect value of the viscosity of air.

His adoption of that incorrect value is another example of the unfortunate influence of authority. This adopted value, 1822.6, was obtained in a doctor's thesis by one of his students [8]. MILLIKAN himself, on page 92 of *The Electron* [5], gives a table of five values of the viscosity, found previous to 1917, with an average value of 1824.0 for which I find a probable error of 0.5. But although Harrington's value thus deviates from this average by three times the probable error of the average, MILLIKAN writes [9], «I give to it alone greater weight than to all the other work of the past fifty years in this field taken together... The error can scarcely be more than one part in two thousand.» Actually, the later work already mentioned (average 1832.45) shows that the error in Harrington's value was some *eleven* parts in two thousand.

The probable source of the error in Harrington's work was finally located by BEARDEN, in 1939 [10], while conducting experimental work on this same constant. He observed that the measured value of the torsion constant of a wire varies with the mass supported, and noted that HARRINGTON had used

an entirely different mass in evaluating the torsion constant from that used in his actual viscosity experiments.

As already noted, I recalculated Millikan's data, in 1929, and I obtained 4.768 in place of his 4.774, using his adopted value of the viscosity of air, which had not at that time been questioned. This decrease of 0.006 in the value of e results from three almost equal corrections, all in the same direction.

In the first place, MILLIKAN measured his voltage in international volts, which differ by about five parts in 10^4 from absolute volts [11]. On the other hand, the absolute coulomb differs from the international coulomb by only some five parts in 10^5 . Since MILLIKAN used international volts, it was apparently assumed by everyone (and is so stated explicitly by HENNING and JAEGER, in the GEIGER and SCHEEL *Handbuch* [12]) that his result was in international coulombs, which differ negligibly from absolute coulombs. But as I pointed out in the 1929 paper, voltage is the *only* electrical quantity actually measured in the oil-drop experiment, and it acts against *mechanical* resistance (viscosity of air), *not* against electrical resistance. The change to absolute volts lowers the value of e by 0.046 percent, or $0.0022 \cdot 10^{-10}$ esu.

Then MILLIKAN used 299900 km/s for the value of c (possibly the most reliable value at the time). Use of any one of the more recent values (roughly 299790) lowers the value of e by 0.037 percent, or 0.00175. The total change thus lowers e from 4.774 to 4.770. The remaining divergence from my final 4.768 is only 0.04 percent, but this change involves one of the most important matters considered in this paper—namely the method of calculation.

As I am certain all of you know, the oil-drop value of e is obtained by plotting an *apparent* value e^3 against $1/pa$, where p is the pressure of the air and a is the radius of the moving drop. MILLIKAN found such a plot, for reasonably small values of $1/pa$, to be strictly linear, and by extrapolation to zero value of $1/pa$ one obtains the true value of e^3 .

The straightforward method of calculation is now to make a least squares solution of the equation $y = a + bx$, and in that way I obtained [13], from Millikan's data 4.7721 ± 0.0038 where he had obtained 4.774. His own method of calculation was to get a value of the slope directly from a *plotted* graph of the data. This is a highly uncertain procedure, as I pointed out in 1929. Every person who makes such a plot will get a more or less different result, and even the same person will get a different result, every time he repeats the process on a given plotted set of data.

MILLIKAN then used the slope thus determined to extrapolate *each* experimental point (25 in all in his 1917 work) to the vertical axis. He thus got 25 values of the intercept, which he then treated as 25 directly observed values of a single unknown quantity and accordingly merely calculated the arithmetic average. He also calculated the probable error in such an average, for n

observations, viz:

$$r_a = 0.6745 \left[\sum r^2 / n(n-1) \right]^{1/2}.$$

He states that his result is the most reliable that can be obtained from the data.

Now, *if* MILLIKAN had obtained the slope, b , of his plot by least squares, then his procedure would have given just the corresponding least squares value of the intercept, a . Thus, in terms of a slope, known or specified, we have, by least squares (for unweighted data),

$$a = (\sum y - b \sum x) / n.$$

Moreover, *if* there is no assumed error in the slope, then the probable error in the intercept is given by the simple equation just stated.

But in Millikan's case there is, of course, an experimental error in the slope, for which one can unfortunately make no objective estimate, when a graphical process has been used to evaluate it. In fact, this inability to make any well-founded, objective estimate of uncertainty is one of the greatest objections to any graphical process. By the foregoing incorrect procedure MILLIKAN obtained, finally, 4.774 ± 0.0018 , whereas the true probable error, resulting from statistical fluctuations only, is ± 0.0038 , as already given, or 2.1 times as large as Millikan's figure.

In his final estimated uncertainty MILLIKAN, for no apparent reason, makes *no* allowance for any such statistical error! He merely assigns a *maximum uncertainty* of 0.07 percent to the value of e resulting from the uncertainty in the viscosity of air, and an equal maximum uncertainty from the measured cross-hair distance. Instead of *adding* these maximum uncertainties (as should have been done) to get final maximum uncertainty, MILLIKAN took the square root of the sum of the squares, and thus obtained his adopted 0.1 percent. In 1929 I decided that the *probable error*, rather than the maximum uncertainty, was at least 0.1 percent.

In this particular case, Millikan's semi-graphical method led to a result that differed from the least squares result by an amount (0.002) that was just half of the calculated probable error of the least squares result. That is a considerably better agreement than might be anticipated. But in his work on h/e , where *only* the slope of a linear plot is desired, he was not so fortunate.

In this beautiful confirmation of Einstein's photoelectric equation [14],

$$Ve = h\nu - p$$

MILLIKAN obtained a value of h (on the basis of $4.774 \cdot 10^{-10}$ esu for the value

of e) of $6.56 \cdot 10^{-27}$ erg s, from his data on sodium, to which he attributed a maximum uncertainty of 0.5 percent. But from these same data, by least squares, one gets 6.469 ± 0.048 , which thus differs from Millikan's value by about *twice* the least squares probable error, and by three times his stated maximum uncertainty. This discrepancy of about twice the least squares probable error is more nearly the purely gratuitous error usually introduced by a graphical method, even when carried out with large cross-section paper of high precision.

As a matter of fact, the least squares solution for the straight line involves such simple equations that it can be calculated almost as rapidly as one can construct an accurate plot. This is quite aside from the lack of any formula for calculating the probable error of a result obtained graphically.

On the other hand, such a plot of the data is always necessary, in a preliminary survey, just to determine the general form of the curve, and to note any points that deviate by an unreasonable amount from *any* smooth curve. It is, I believe, just the blind use of least squares methods, without such a preliminary graphical survey, that has sometimes led to absurd results and consequent doubts regarding the validity of the method.

It may be noted, incidentally, at this point that the closely related equation

$$h\nu = Ve$$

as used in connection with measured excitation and ionization potentials, furnishes the illustration of an inconsistency mentioned earlier, namely the use of two *different* values of c in the *same* equation. Thus the frequency ν (s^{-1}) is obtained from the measured wave number (cm^{-1}) by multiplication by c . Similarly the potential V (esu) is obtained from the measured voltage by multiplication by $10^8/c$. Thus the factor c^2 enters the actual working equation.

But when I was writing my 1929 paper I discovered that it was only too customary for the best available value of c to be used in obtaining actual frequency, but for 300 to be used in place of the correct $c/10^2$ in the voltage transformation. Aside from this glaring inconsistency, the latter approximation introduces an error of 0.07 percent, which was by no means negligible even in 1929. But although I emphasized this point in my paper [15], the same error has actually occurred, even many years later and in connection with work of the highest precision.

If investigators would only write an expression for any result, *explicitly* in terms of the quantities actually measured (which in the foregoing illustration would lead to the explicit appearance of the factor c^2), inconsistencies and unjustified approximations would be far less likely to occur.

3. – Velocity of light.

As already noted, my 1941 paper [1] included details on the velocity of light only, and I have always been particularly interested in the determinations of this fundamental important constant. Certainly no constant has had more, and more extended work devoted to its evaluation.

As all of you know, the first direct terrestrial measurement of the velocity of light was made in 1849, by FIZEAU, with his toothed-wheel apparatus. He was followed in 1850, 1862 by FOUCAULT, with his revolving mirror. Neither man published any diagram of his apparatus and this omission, especially in the case of Foucault's work, has resulted in many incorrect diagrams and statements in subsequent articles and text-books, the details of which are obviously inappropriate here [16].

Refined work, using a rotating mirror, was started by A. A. MICHELSON in 1878, while he was an instructor in physics at the U. S. Naval Academy at Annapolis, Md. The Superintendent of the Academy had so low an opinion of such work that he once told MICHELSON that he would never amount to anything because he wasted his time on such useless experiments! But MICHELSON did get a Nobel Prize for such work, while the name of the superintendent seems lost in oblivion.

By a clever modification of Foucault's experimental arrangement, MICHELSON increased the intensity of his observed beam of light by more than six times over that which would be obtained with a Foucault arrangement of equivalent size. It is in connection with that sort of thing that MICHELSON was a genius. But he was not a theoretical physicist, and in his first article [17] MICHELSON apparently thought that he had obtained a parallel beam of light, and that the observed intensity of the light reflected by the distant mirror was independent of the distance, an obvious error that has since been repeated in at least one authoritative source [18]. But MICHELSON corrected this misconception in his subsequent papers.

In spite of Michelson's experimental genius, he apparently overlooked some fairly obvious sources of error, as has been pointed out by DORSEY [19], in his long critical paper on the velocity of light. DORSEY states (p. 54 loc. cit.) « Most unfortunately, his reports on the velocity of light, late as well as early, are marred by ambiguity in expression, are deficient in essential details, and give no evidence of any serious search for systematic errors. »

DORSEY discusses in great detail some of these sources of error, nearly any one of which *may* have been as large as Michelson's estimate of the final uncertainty in his result. In this 1879 work Michelson's final result was (299910 ± 50) km/s, in which the 50 km/s was intended to represent more of

a «limit of error» than a probable error. His result, as we now know, is actually in error by about 117 km/s.

The chief reason for the foregoing remarks is the possible bearing that they have on the 1932-1933 work of MICHELSON, PEASE and PEARSON [20] using a mile long evacuated tube, laid on the ground near Santa Ana, California. The average of their 2885 observations, for which the reduction to vacuum is negligibly small, is 299 774 km/s. I found, in connection with the writing of my 1941 paper, that the 2885 observations do not follow a Gaussian error distribution, but that the actual distribution can be approximated most simply by the sum of two Gaussian distributions, with standard deviations (for a single observation) of 5 km/s and 15 km/s, respectively. Since the former figure is roughly the expected value, it seems obvious that there are systematic errors, presumably of widely varying magnitude, affecting a great part if not all of the work. But since the observed distribution is quite symmetrical, I assumed, in 1941, that the *average* value was fairly reliable, and I assigned to it a probable error of 4 km/s. We now know, however, from the very precise recent work, that the actual error is some 19 km/s.

The cause of this large systematic error (6 parts in 10^5) is still unknown. The error in the final result can scarcely be in the measured length, since it corresponds to the relatively huge amount of some 9 cm in the measured mile. It must therefore be in the measured time interval. This last figure depends on the rate of rotation of a mirror with 32 sides (giving close to null displacement of the image) which, by a rather elaborate transfer process, was finally checked against the standard time signals sent by wireless four times a day from Arlington, Virginia. It is obviously impossible now to track down systematic errors in such an involved procedure. More modern methods of measuring the velocity of light, which make use of standard frequency broadcast signals, have in this respect an enormous advantage over earlier work. In fact, the time measurement, with an error in frequency not exceeding a few parts in 10^7 , should be more accurate, if anything, than the measurement of distance [21].

The final value of the velocity of light, adopted in my 1941 paper, was $(299\,776 \pm 4)$ km/s. This happened to be just the value and uncertainty I had suggested in 1934, in a brief letter to *Nature* on this important constant [22]. But the 1941 table of values included also the 1937 and 1940 work of ANDERSON [23], and the 1937 work of HÜTTEL [24], both of whom used the interference phenomena produced by a light beam modulated in intensity by a Kerr cell. The final average also included, as it did in 1934, the old (1906) but extremely careful determination by ROSA and DORSEY [25] of the ratio of the magnitude of an electric charge, measured in e.s. units, to that of the same charge, measured in e.m. units.

The weighted average of eight determinations, as calculated in 1941, was 299 776.4 km/s, with a probable error of only 1.5 km/s, on the basis of external

consistency, of 2.7 km/s, on the basis of internal consistency. Thus these eight results, obtained by *six* different investigators, using *four* completely different experimental methods, agreed with one another, on the average, *twice* as well as was to be expected on the basis of the probable errors that had been assigned to the individual results. Under such circumstances one would expect that the final average could almost certainly be trusted to the indicated uncertainty. In other words, all the different methods are subject to systematic errors; for example, the electron multiplier tube used by ANDERSON (loc. cit.) in his Kerr-cell apparatus had an admitted instrumental defect, resulting from differing transit times for the electrons produced by the two interfering light beams, a defect that has now been eliminated by BERGSTRAND in his so-called «geodimeter» [26]. But one would scarcely anticipate that the several final systematic errors should all be in the *same* direction and of roughly the *same* magnitude.

We are, however, now fairly certain that the true value of the velocity of light is close to 299793 km/s, and hence that the 1941 average is in error by fully *four* times its assigned probable error. What makes this result the more remarkable is the fact that it is the *only* one of my 1941 adopted values of important constants that differs from the present best value by more than might be expected, on the basis of the uncertainty assigned in 1941. As a matter of fact, in the case of ten of the most important atomic constants (N , e , m , h , λ_0/λ_s , F , e/m , h/e , α , and M_p/m), *no one* of the adopted 1941 values differs from the latest values of DuMOND and COHEN by as much as the assigned probable error. The *average* discrepancy is only 55 percent of the assigned probable error whereas, by the theory of errors, it should *exceed* the probable error by roughly 20 percent.

Thus the measured values of the velocity of light have shown an almost unique variation with time. In fact, as I discussed in my 1941 paper, DE BRAY in a series of articles between 1927 and 1934, mainly in *Nature* [27], insisted that the value of c was decreasing with time at a truly alarming rate—one that would lead to a value of zero in a mere 75000 years!

It is certainly a fact that the series of observations by CORNU-HELMERT, MICHELSON, and NEWCOMB, in the period 1875 to 1885, gave an average result of closely 299900 km/s, which is too large by some 110 km/s, over twice the uncertainty assigned at the time. Then in the period 1923 to 1940, but including the result obtained in 1906 by ROSA and DORSEY [25], the results averaged 299776, a value smaller than the previous by 124 km/s, but *now too small* by fully 16 km/s. Thus the measured values of the velocity of light have not only stopped decreasing—they have now *increased* appreciably.

In fact all but one of the latest results, as tabulated by DuMOND in the paper he is to give, are larger than 299790 km/s. My own present estimated best average is 299792.4 km/s, which seems to deserve a probable error of

not more than 1 km/s. This estimate includes the very recent work by EDGE [28], using Bergstrand's «geodimeter» method. Unfortunately this report appeared too late to be included in the very extensive calculations of DuMOND and COHEN that will be presented to this conference. But BERGSTRAND, himself, will present his latest results.

This tendency of a series of experimental results, at a certain epoch, to group themselves around a certain value raises a very interesting psychological question. Dr. E. O. LAWRENCE, from his own experimental experience, once gave me the following possible explanation. In any highly precise experimental arrangement there are initially many instrumental difficulties that lead to numerical results far from the accepted value of the quantity being measured. It is, in fact, just such wide divergencies that are the best indication of instrumental errors of one kind or another.

Accordingly, the investigator searches for the source or sources of such errors, and continues to search until he gets a result close to the accepted value. *Then he stops!* But it is quite possible that he has still overlooked some source of error that was present also in previous work. In this way one can account for the close agreement of several different results and also for the possibility that all of them are in error by an unexpectedly large amount.

But such an argument is no longer valid when two or more completely different methods of experimentation have been used, which cannot possibly have a common source of systematic error. It is for just this reason that it is so essential to measure any important constant by quite different methods, if that is in any way possible. But these remarks leave the «low» 1941 value of the velocity of light just as much a mystery as ever.

4. — Group and wave velocity.

One of the most unusual, and one of the most interesting errors I encountered in the literature was the use of the *wave* index of refraction of air, in place of the correct *group* index, in connection with the evaluation of the velocity of light in vacuum. This situation also illustrates the all too common ignorance displayed by investigators of previous work in the field. Fortunately, with the appearance of very complete abstracting journals in recent years, it is now far easier to obtain a complete history of relevant previous work than it was a half century or more ago.

This matter of group velocity is considered in G.C. 1941 [1], pages 93 and 94, but although I had then spent a considerable amount of time delving into history, I did not discover some of the most interesting aspects of the subject until shortly *after* that paper was in print. Accordingly, in order to make certain corrections in that paper, and especially in order to give proper

credit to those concerned, I am now presenting the following rather full details.

In discussing the 1927 work of MICHELSON [29], at Mount Wilson, and his reduction of the velocity of light from air to vacuum, I wrote [1]:

« It is easy to show that his correction results from the use of the *wave* index of refraction, instead of the correct *group* index of refraction.... It is well known that MICHELSON, about 1883, obtained 1.330 for the index of refraction of water, and 1.76 ± 0.02 for the index of CS_2 , by a direct comparison of the velocities (of white light) in air and in the two media mentioned.

« Now the *wave* index of refraction of CS_2 is 1.624 for the "D" line, and 1.637 for the "E" line. To explain his high observed value for CS_2 , MICHELSON employed the concept of *group* velocity (and the corresponding *group* index of refraction), as discussed in connection with the velocity of light by RAYLEIGH [30]. For CS_2 the group index μ_g is 1.722 and 1.767 for "D" and "E" lines respectively, in good agreement with Michelson's observed result. This is, however, the *only* instance in which MICHELSON ever used the concept of group velocity! He never applied it to his work on the absolute value of c , and neither has anyone else working in the field, until I called Dr. Anderson's attention to the matter [31] several years ago. MICHELSON did not even apply group velocity to his observed index for water. If he had, it would have spoiled the apparent agreement, for the group index is 1.352 and 1.359 (for the "D" and "E" lines), whereas the wave index is 1.334 and 1.336, as compared to his observed 1.330. »

In a footnote I wrote also that MICHELSON found that in CS_2 « orange-red » light (which he assumed as 6200 Å) travels one to two percent faster than « greenish-blue » light (assumed as 4900 Å), a result that had since been regularly quoted as in good agreement with theory. I then gave rough figures for the actual calculated change in the *group* index. More exact magnitudes are as follows.

Michelson's actual result for the difference in velocity was 1.4 percent, and his 13 individual measurements vary from 0.6 percent to 2.0 percent with an average deviation from the average of 0.4 percent. Now the calculated change in the *wave* index of CS_2 , from 4900 to 6200 Å, is 1.8 percent. But the equation for the group index is

$$\mu_g = \mu - \lambda_0 \frac{d\mu}{d\lambda_0}.$$

When this is combined with the equation for the wave index

$$\mu = A + \frac{B}{\lambda_0^2} + \frac{C}{\lambda_0^4} + \dots$$

it follows immediately that, to a first approximation, the *variation* in the group velocity, for a given short interval of wavelength, is just *three* times

that in the wave index. A more accurate calculation gives 5.08 percent as the change in the group index that MICHELSON should have found.

The corrections I now wish to make in my 1941 paper are the following. In the first place, MICHELSON *never* personally used the group index of refraction for anything, not even for his work with CS_2 ! In the second place, I was not the first one to point out the discrepancy in Michelson's measured index of refraction for water. Credit for that should go to J. WILLARD GIBBS. In the third place, I was not the first one to call attention to the possible use of the group index, in connection with the measured velocity of light in *air*. Credit for that goes to Lord RAYLEIGH.

Full details of Michelson's 1882-1883 work in Cleveland on the velocity of light, including the work with water and carbon disulphide, were not published until 1891 [32], although the paper is dated 1885 and includes an introductory note by NEWCOMB (dated April 1885), who described his own measurements made in 1880-1882 in a very long paper (pp. 107-230) in the same volume. MICHELSON, in his paper, never mentions group velocity and has no explanation to offer for his high value of the index of refraction for CS_2 . But NEWCOMB, in his introductory note to MICHELSON's paper, does refer very briefly to the theoretical work of Lord RAYLEIGH on group velocity, although he gives no figures.

NEWCOMB makes slightly more extended remarks in his own paper (p. 201, loc. cit.), probably written also in 1885. He states: «The suggestion of Professor Lord Rayleigh that the group velocity of light in air, which is the quantity actually measured, may be less than the true wave velocity, has received a certain amount of confirmation from the researches of Professor Michelson on the velocity of light in bisulphide of carbon. This result shows that the actual reduction to vacuum should be greater than that deduced from the index of refraction. But Michelson's measures show the correction to be too small to be taken into account. We therefore adopt 1.000273 as the factor of correction.»

This last figure is the wave index of air under *standard* conditions (15 °C, 760 mm), *not* under the actual conditions of pressure and temperature of any given experiment. It corresponds to a correction of 83.0 km/s in the velocity of light. Use of the correct group index gives 85.7 km/s for the correction, a difference of only 2.7 km/s, which was obviously negligible in work having an estimated uncertainty of at least 50 km/s. But this difference is certainly not negligible in modern work. Furthermore, in the Kerr-cell method for determining the velocity of light, as used by ANDERSON [31] and others, the difference of group and wave velocity amounts to the much larger figure of some 7 km/s, as a result of the presence of a certain amount of glass and nitrobenzene in the light path.

Actually, Newcomb's use of standard conditions of temperature and pres-

sure can cause a far larger error than that just mentioned. Thus in Michelson's Mount Wilson work [29], carried out at an elevation of 6000 feet or more, his correction was only 67 km/s, or 16 km/s less than the calculated value for standard conditions.

Then in 1886 J. WILLARD GIBBS [33], in a review of the work of NEWCOMB and of MICHELSON on the velocity of light, gave a complete quantitative discussion of this matter of group velocity. That the GIBBS article was entirely overlooked by subsequent writers and investigators probably resulted from the fact that it was merely a review note and was signed merely with the initials « J.W.G. »: GIBBS regularly reviewed important papers for the *American Journal of Science*, signing these reviews with his initials, as is quite customary in such cases.

GIBBS writes: « Professor Michelson's experiments on the velocity of light in carbon disulphide afford an interesting illustration of the difference between the velocity of waves and the velocity of *groups* of waves — a subject which is treated at length in an appendix to the second volume of Rayleigh's *Theory of Sound* ». GIBBS then uses Verdet's constants for CS₂ and finds for the "D" and "E" lines just the group index values I have already quoted from my 1941 paper. GIBBS *also* calculated for *water* just the group index values that I listed, and commented on their poor agreement with Michelson's experimental value.

However, GIBBS did fail to notice that Michelson's *change* of index for CS₂, for the 4900 to 6200 Å interval, was in utter disagreement with the calculated value for the group index, just as practically every one else seems to have done. One exception was BOUASSE, who in his 1935 text on the propagation of light [34] gave a long and involved original derivation of the group index of refraction, making an error somewhere in the derivation and coming out with a result incorrect by a factor of two. He thus obtained 9.6 percent for the calculated change in CS₂, a result that left him completely mystified!

But another French physicist, C. GUTTON, had shown conclusively, 24 years earlier [35], that the variation in the velocity of light with wavelength in CS₂ (he measured no absolute values) agrees perfectly with the *group* index equation. A full account of GUTTON's work, and a reproduction of his plotted experimental results was given by R. LADENBURG [36], in 1928. But LADENBURG seemingly also failed to notice the glaring discrepancy of these results with Michelson's data on the *change* of velocity in CS₂.

In concluding this topic I note that whenever the *velocity* of propagation of *energy* is being measured, the group velocity and the group index of refraction applies. But in the case of all stationary *interference* phenomena, which occur as a result of the *wave* character of light, the wave index of refraction is to be used. From these latter phenomena one can determine only

the *wavelength* of visible light (and its reciprocal, the wave number), and never its velocity of propagation, so long as the frequency is unknown.

5. - The Avogadro number, N .

Because of the special significance of the Avogadro number for this conference, its value will be considered with some care. It is numerically the largest of the universal constants, but in spite of its huge size (*), the latest DuMond and Cohen value, $N = (6.02486 \pm 0.00016) \cdot 10^{23}$ mole⁻¹, has thus an estimated standard deviation of only one part in 40000. This constant not only is the largest, but it has been evaluated by the largest number of different methods of any of the universal constants.

The Avogadro number is frequently called the Loschmidt number (especially in German references), on the ground that Avogadro himself never made any estimate of its numerical value. It is claimed that such an estimate was made first by the Viennese physicist Loschmidt [37], nine years after Avogadro's death, on the basis of the kinetic theory of gases. This method yields only a lower limit for the value, and in 1909 Perrin obtained in this way $N > 4.4 \cdot 10^{23}$. But the term « Loschmidt number » is frequently reserved for the number of molecules in one cm³, whereas the term « Avogadro number » nearly always refers to the gram-mole, for which the standard volume is roughly 22.4 liters. We shall, as in the past, employ these last definitions. Moreover, this definition of the Avogadro number N has recently been approved by the Commission for Symbols, Units and Nomenclature, of the International Union of Pure and Applied Physics (meeting in Paris, March 1956).

Virgo [38] in 1933 wrote an interesting summary of all experimental work on the Avogadro number, up to that time. He lists 72 different results, obtained by no less than twenty different methods. Because, however, of the relative inaccuracy of even the best of the direct methods of measurement, it was then customary to calculate N indirectly from the adopted values of the faraday and the electronic charge ($N = F/e$).

But a few years later one of the direct methods had been developed to the point where the resulting value of N was probably more accurate than that obtained indirectly from the oil-drop value of e . Hence in recent years N has been treated as a *primary* constant, and e as a *derived* constant ($e = F/N$). This method for evaluating N involves a knowledge of the wavelengths of X-ray lines, both by ruled gratings and by crystal reflection, combined with

(*) To count even the number of molecules in one cm³ of a gas under standard conditions, at the rate of ten per second, would require 85 billion years, which is some twenty times the estimated age of the universe.

the known density, molecular weight and geometric structure of the reflecting crystal.

In the G.C. 1941 [1], I thus calculated $N = (6.0245 \pm 0.0011) \cdot 10^{23}$ mole⁻¹, on the chemical scale, from data on calcite only. But during the period 1940 to 1944 very accurate density measurements on several crystals appeared, and in 1945 [6] I made a critical study of the value of N yielded by five different crystals (calcite, rock salt, diamond, LiF and KCl). The surprisingly consistent values of N given by the five different crystals seem to show that the assumption of a geometrically perfect structure for the specimens used is valid to at least one part in 10000. There had previously been much dispute concerning this last assumption.

The weighted average of the five results is 6.02338 ± 0.00023 , on the basis of internal consistency errors, and only half that probable error, from external consistency. But the internal consistency error just quoted includes no allowance for the largest source of error in the evaluation of N , namely the conversion factor from the SIEGBAHN to the c.g.s. (or absolute) system of wavelengths. A full table of the experimentally determined values of this transfer factor λ_o/λ_s (now denoted A by DUMOND and COHEN, a symbol that will be adopted here), was given in the 1945 paper. The average value was found to be 1.002030 ± 0.000020 , i.e., a probable error of two parts in 10^5 .

But that table unfortunately did not include the final results of TYRÉN's work [39], which were unavailable and unknown to me at the time. I had therefore included only his preliminary value [40]. TYRÉN's final work yields four resulting values of A , varying only from 1.00195 to 1.00202, with a weighted average of 1.001988 ± 0.000017 . (This uncertainty is based on statistical fluctuations only). When this new determination, with what appears appropriate relative weighting (*), is included with my other 1945 data one gets a final weighted average of 1.002017, to which I again assign a probable error of ± 0.000020 , which seems a liberal estimate. This last weighted average result was obtained in April, 1945.

Meanwhile, in 1943, the British X-ray Society (X-ray Analysis Group of the Institute of Physics, W. L. BRAGG, Chairman) had decided officially to record henceforth all X-ray wavelengths in absolute (c.g.s.) units, instead of the customary Siegbahn units [41]. This decision required the adoption of an official value for the ratio A to be used in converting all previously published X-ray wavelength values. It was voted to leave the decision on such a value to Dr. BRAGG and the chairman (B. E. WARREN) of the corresponding American organization (Amer. Soc. for X-ray and Electron Diffraction, or ASXRED), in consultation with Professor M. SIEGBAHN and myself.

(*) Weights: All BEARDEN work 16.97, BÖCKLIN 2.78, SODERMAN 1.42, and (new) all TYRÉN work, 10.85.

After considerable correspondence during the years 1944 and 1945, the value 1.00202 was chosen, with a standard deviation of three parts in 10^5 , in agreement with my own calculated value of 1.002017 to which, as just noted, I had assigned a probable error of two parts in 10^5 (or a standard deviation of three parts in 10^5). The question of probable error versus standard deviation will be discussed in the next section of the paper. I merely note, at this point, that since I have used probable error as an estimate of uncertainty in all my previous articles, it is convenient to retain that form of estimate, in discussing such work. In all DuMOND and COHEN articles during the past five years, the indicated uncertainties of their « output » values represent standard deviations. But again, for convenience of comparison, I have here when necessary reduced such uncertainties to probable errors, by multiplication by 0.674 5, a figure that applies *only* to a Gaussian error distribution.

Official action on the value of A was taken by Bragg's group in July 1946 and this action has been published in many places [42]. With the new 1.00202 value, in place of 1.00203, but with the same crystal data as were given in the 1945 paper, the value of N is *raised* from 6.023 38 by *three* parts in 10^5 (since the cube of A is involved), and hence to 6.023 56 on the chemical scale, or to $6.025\,20 \pm 0.000\,43$ on the physical scale (using the conversion factor $r = 1.000\,272$ for the two scales of atomic weights). No change of probable error occurs, since that assigned to A remains unchanged.

Very recently, in fact since the writing of this paper was completed and typing started, DuMOND and COHEN have noticed that Tyrén's values of A are definitely subject to corrections arising from the Lamb shift, which was entirely unknown at the time of TYRÉN's work. Their tentative corrected Tyrén result is close to the Bearden value of 1.002 03. They will doubtless mention this new development in their own papers, which follow. Since my own calculations have already been completed, I am leaving them unchanged, except for an important inserted remark at the end of this Section.

Quite aside from this question of the value of A , there are now available additional crystal data. BROGREN [43] has made careful measurements on calcite and on quartz crystals. In order to avoid what he claims is an uncertainty associated with the determination of β , the angle between the edges of the calcite rhombohedron, BROGREN measures two additional crystal spacings, by the same method (X-ray reflection) as that used for the well-known calcite crystal spacing d . In this way the unit cell volume can be computed, quite independent of the measurement of any crystal structure angle. He thus obtains $N = 6.02327$. He also measured β and from the resulting value of d he obtains $N = 6.02329$, a remarkably close agreement. These values are on the chemical scale, with the use of $A = 1.00202$ and $r = 1.000\,272$ (for calculating the *chemical* atomic weights from *observed* atomic masses of the physical scale).

He also obtains a much higher value (6.02368) of N from quartz, but this result is untrustworthy since he uses the molecular weight of pure SiO_2 but has no chemical analysis of possible impurities in his quartz crystal. In fact, he criticizes the result for NaCl that I used in 1945, on precisely the same grounds. I used (and specifically admitted, in my paper) the grating space of rock salt, combined with the density and molecular weight of pure NaCl (*).

Just because of this valid criticism, it seems best now to omit my NaCl value of N . The new average is then 6.02505 (physical scale), in place of 6.02520. The average of Brogren's two values for calcite is 6.02328 on the chemical scale, or 6.02492 on the physical scale. If this value is given the same weight as my almost identical (6.02496) 1945 calcite value, and is then combined with my remaining four crystal values, the new weighted average is 6.02501, with a probable error of ± 0.00020 by internal consistency, and only 18 percent of that by external consistency! These last two figures may be compared with ± 0.00023 and 47 per cent found in the G.C. 1945 [6] paper.

But just as was the case in 1945, much the largest contribution to the final probable error in N comes from that in A . This error (60 parts in 10^6), when combined with the *internal* consistency probable error just quoted, gives finally, $N = (6.02501 \pm 0.00041) \cdot 10^{23} \text{ mole}^{-1}$, which replaces the $(6.02520 \pm 0.00043) \text{ mole}^{-1}$ of the 1945 paper (physical scale, $A = 1.00202$, $r = 1.000272$).

Now DuMond and Cohen, in their extensive calculations made during the past several years, have always used just my 1945 value of N as «input» data. Since the shift from 6.02520 to 6.02501 is less than half the assigned probable error, this shift, if made, should produce no significant change in their final «output» value. Actually, in order to treat A as well as N as one of the unknowns, DuMond and Cohen free the crystal value of N from the influence of A by calculating NA^3 , using my 1945 value of N ($= 6.02502$ on the physical scale) and $A = 1.00203$. The result, 6.06179, then represents the weighted average of my 1945 crystal data, before transfer from the Siegbahn scale by the use of $A = 1.00203$. In agreement with a suggestion by DuMond and Cohen, NA^3 may be termed the «Siegbahn-Avogadro number, N_s .» They then use the officially adopted $A = 1.00202 \pm 0.00002$ as another item of their «input» data.

(*) BROGREN never states explicitly what final value of N from calcite was used. But his stated weighted average (6.02336) for calcite and quartz, combined with his single quartz value and with his adopted relative weights of 2 to 1, corresponds to a value of 6.02320 for calcite. It may also be noted that he quotes an incorrect equation for β in terms of α (the three equal obtuse dihedral angles of calcite), the same incorrect equation printed (but obviously not used) earlier by BEARDEN [*Phys. Rev.*, **38**, 2089 (1931)] to which I called attention in footnote [21] of G.C. 1945 [6].

In their 1953 and 1955 calculations, to be presented at this conference, their « output » value of N_s is 6.06179, *identical* with the « input » value. Thus the use of all the related data considered by these investigators, many combinations of which can be shown to lead to more precise values of N than that derived directly from crystal data [44], makes no final change in the calculated Siegbahn-Avogadro number.

But their *separate* output values of N and A do not agree quite so well with their input data. Thus they obtain 1.002039 ± 0.000010 (probable error) for the *output* value of A . In the case of N no direct comparison is possible since the *input* quantity is not N but $NA^3 = 6.06179 \pm 0.00023$ (probable error). This corresponds to $N = 6.02520 \pm 0.00023$ (my 1945 value, *without* allowance for error in A^3 , with $A = 1.00202$). Their output value of N is 6.02486 ± 0.00011 (again probable error). Thus the output and (*effective*) input values of N differ by 150 percent of the (*effective*) input probable error, and the output and input values of A differ by 95 percent of the input probable error. COHEN [45] has recently given the results of a rigorous calculation of the standard deviations of the *differences* between the input and output values of all of the DuMond and Cohen constants.

STRAUMANIS [46] also has noted the close agreement between the input and output values of N_s . Presumably, as he states, crystallographers will continue to use their officially adopted value of $A = 1.00202$, in order to obtain X-ray wavelengths in c.g.s. units. A problem then arises whenever the value of N is involved. The most reasonable solution of this problem appears to me to be as follows:

When one is working on any problem concerned only with crystal structure, and is using data, the calculation of which has *already* involved the use of the factor 1.00202, then if for any reason the value of the Avogadro number enters into the work, the most logical value to use is 6.02501 ± 0.00041 , which represents my present best estimate from crystal data after transfer, using the 1.00202 factor. Only in that way can one retain a truly self-consistent set of crystal structure data.

But if one is using N in any general way (e.g., to calculate the value of e , from the equation $e = F/N$), then the most reliable value to use is that given by DUMOND and COHEN, which is based on *all* experimental material in which N is in any way involved. This latter value, as just quoted, is now $(6.02486 \pm 0.00011) \cdot 10^{23}$ mole⁻¹, a probable error that is only 27 percent of that which I have attached to the crystal structure value. One thus sees explicitly the very substantial improvement in precision that can be obtained by the use of all theoretical relations involving N , in place of merely the one that employs crystal data.

Finally, if the best observed value of A is indeed at least as high as 1.00203, as now seems quite likely, then my latest crystal value of N is lowered from

6.02501 to 6.02483, in essentially *exact* agreement with the present DUMOND and COHEN value of 6.02486. Moreover, if these investigators use 1.00203 as a new «input» value of A , the «output» value of N in their general solution will be lowered to 6.02480, on the basis of information just sent to me by Dr. DUMOND. Thus the «problem» just mentioned vanishes completely — a most happy ending of a long story.

6. — The fine structure constant and the representation of experimental uncertainty.

The late A. S. EDDINGTON, one of the most philosophic of modern physical scientists, in 1929 derived by what he considered purely logical reasoning a value of 136 for the reciprocal of the fine structure constant [47], which he believed at the time to be in good agreement with the latest experimental value. After I had called his attention [48] to the fact that the new value, like the old, was actually close to 137, and *not* to 136, he reviewed his reasoning and concluded [49] that he had overlooked one (so-called) «degree of freedom» and that his calculated value was in fact 137.

In 1929 I gave as the most probable value [50] $1/\alpha = 137.29 \pm 0.11$. In 1941 the experimental value had come much closer to 137, but the uncertainty had become much less. It was then [51] $1/\alpha = 137.030 \pm 0.016$. The latest DUMOND and COHEN value is 137.0373 ± 0.0004 . Thus in spite of the close approach to 137, it is now quite evident that $1/\alpha$ is *not exactly* 137 and in my opinion there is no good reason why it should be. I do not believe in Numerology.

In 1933 EDDINGTON published a very curious paper entitled: «Notes on the Method of Least Squares» [52]. This is not only a curious paper, it is also one that is factually incorrect in certain aspects which, however, lie outside the scope of this talk. It is evident that, at the time, Eddington's knowledge of modern statistical theory was rather incomplete.

It is my suspicion that the primary incentive for Eddington's paper was the conclusion of many scientists that the experimental value of $1/\alpha$ could not possibly be 137. As I have just noted, my own 1929 value deviated from 137 by 2.6 times the estimated probable error. But the odds, on the basis of a Gaussian distribution of errors, that the true value deviates from the observed value by at least 2.6 times the probable error are one in 12.6 and a statistician does not usually consider a deviation significant unless the odds are at least 20 to 1 against it. Hence there was, at that time, no clear presumption of evidence against the 137 value.

In this case I think EDDINGTON was irritated because many persons had viewed an estimated «probable error» as though it were a «limit of error».

and hence drew a false conclusion when the proposed Eddington value was observed to lie outside the region thus defined. In fact, EDDINGTON writes: « The practice of allowing merely the probable error as margin is not unknown... a tacit admission by the perpetrator that his habit is to tell the truth only on alternate occasions. »

This remark I consider an entirely unwarranted libel against scientists in general, and is worthy of further comment. In the first place, a statement of the measured or calculated value of any quantity in science is quite meaningless unless accompanied by *some* estimate of its uncertainty. This is a point I have tried to emphasize in all of my work on the general physical constants.

In the second place, in stating such an uncertainty all a scientist can do is to state the *odds* that the true value lies *within* the region defined by the announced uncertainty. If, as is usual, one assumes a Gaussian distribution of errors, then the odds are *even* in the case of « probable error ». They are 2.2 to 1 in the case of « standard deviation » (S.D.). They are 4.6 to 1 for double the probable error, etc. Provided a person states clearly the intended meaning of his listed uncertainty, it is quite immaterial what measure of uncertainty is adopted. When a scientist lists a so-called « limit of error », what he is really trying to say, I believe, is « I think the odds are at least 100 to 1 that the true value lies within the specified range », or maybe « 1000 to 1 ». The first region is given by 3.8 times the probable error, the second by 4.9 times the probable error.

Such statements are even more uncertain than just indicated. For we never know the *true* errors of individual measurements. We know only their deviations (residuals) from some calculated average value. Hence we can state only an estimate of probable error, or of S.D., etc., and a corresponding *estimate* of the odds to be attached to the stated measure of uncertainty. But *any* estimate, no matter how fragile its foundation, is better than none at all, and as pointed out in Sect. 3 of this paper (on the velocity of light), the latest work on the universal constants shows that the estimates of probable error made 15 years ago were at fault only in being, with the exception of that for the velocity of light, nearly double the true error of the adopted value.

It has always been common practice among statisticians and biological scientists, and it is now becoming more common among physical scientists, to use S.D. as a measure of uncertainty. One advantage of S.D. is that it can be calculated for *any* distribution of errors, whereas probable error applies only to a symmetrical distribution. The point to emphasize, in this connection, is that a definite formula for the calculation of probable error exists only for a definite postulated distribution. Moreover, although no such formula is needed for S.D. (it is merely the root-mean-square error and, geometrically, measures the radius of gyration of the distribution curve, for revolution about

an axis set at the chosen value of the measured quantity), there can be no definite odds attributed to S.D. without a postulated error distribution. Similarly, the ratio 0.6745 of the magnitude of probable error to that of S.D. applies *only* to a Gaussian distribution.

I have, in principle, no personal objection whatever to the use of S.D., but the change from probable error will, and already has, led to technical misstatements. Thus uncertainties stated as estimates of probable error (like my own) have been used, in combination with other results, as though they were estimates of S.D. Actually such estimates are nearly always so uncertain that it makes little difference whether they are interpreted as probable error or as S.D. But in assigning *relative weights* to the results of various investigators, it is neither just nor logical to confuse the two. Thus, in order to avoid such confusion, and in particular to facilitate comparison with my previous work, I have in this paper continued to use an estimate of probable error as a measure of uncertainty.

7. - The general system of universal constants.

If I may be pardoned a personal reference, in a paper already far too personal, I believe I was the first to attempt to calculate a set of values of the universal physical constants that was as consistent as possible with the various accepted theoretical relations between them. As a matter of fact, only a portion of such constants have ever been measured directly, or at least measured directly with any precision. Thus the mass of the electron was, some decades ago, always calculated from the measured values of e/m and e .

Very often *functions* of universal constants (of which e/m and h/e are very simple examples), can be measured with much greater precision than the individual constants. The formula for the Rydberg constant, in terms of e , h , m and c is an especially noteworthy example, since even at the time when Bohr first derived it [53], the spectroscopic value that he used for the Rydberg constant was in error by only 0.005 percent, whereas his calculated value differed from it by 5.8 percent, as a result of errors of one to two percent in the values of e , h , and e/m that he used. The enormously increased accuracy of the present calculated value will be discussed later.

One of the most desirable but difficult objectives is to get an overall picture of the prevailing agreement or lack of agreement between the various measured functions of the universal constants. To make such a picture possible, I adopted an idea first suggested by BOND [54], and generalized it to construct a nomographic chart. The great advantages of any nomographic chart for showing, at a glance, all possible numerical relations between a series of simple

functions of certain basic quantities are too well known to merit repetition. Because of lack of time I shall not go into the details of this chart, which I used first in my 1932 paper [55]. Later the designation « Birge-Bond diagram » was suggested by others and has since appeared commonly in the literature.

Since any such chart is plotted in two dimensions, only two independent variables (unknowns) are possible. I employed *three* such variables, e , m and h , but eliminated m , wherever present, by use of the Rydberg constant formula just mentioned. Another thing that was done, I believe for the first time, in that 1932 paper was to calculate the *probable error* of each *function* of e , m and h , whose value had been determined by a least squares solution. In the case of a nomographic chart like that under discussion, *any* straight line, $y = a + bx$, gives a possible consistent relation between values of all the functions represented.

Now the appropriate equations for calculating the probable errors of functions of *independently* observed quantities are well known. In the case of a first degree polynomial the formulae for the probable errors of the *coefficients* a and b of the equation, as *simultaneously* evaluated by least squares, are also well known. In fact, I listed these formulas in my 1929 paper, as already mentioned in Sect. 1 of the present paper.

What has been until recent years far less well known is the general formula for the probable error of *any* function, the coefficients of which have been simultaneously evaluated by least squares, even though such a formula was derived by GAUSS, in his original work on least squares [56]. The formula is, in general, quite laborious to work with, since it involves all elements of the matrix of minor determinants of a set of simultaneous linear equations, whereas the probable error of each of the successive coefficients of these linear equations involves successively only a single element of the main diagonal of the matrix.

In 1932 I had never seen the calculation of the probable error of such a function carried out by any physical scientist, although the late HENRY SCHULTZ (a statistician) had given, in 1930, a detailed account of the derivation of the general Gauss formula and of its application to a typical problem in statistics [57].

But the problem is enormously simplified when the function is a polynomial, as I suddenly realized and pointed out in my 1932 paper on least squares [58]. It is especially simple in the case of the first degree polynomial, $y = a + bx$, as used in the Birge-Bond diagram. Thus it is obvious that the probable error in this function (or in *any* polynomial), at $x = 0$, is merely the probable error r_a in a . It should be equally obvious that, by transforming the original equation to $y = a' + b'x'$, where $x' = x - \varepsilon$, the probable error in a' gives the probable error in the function at $x' = 0$, or $x = \varepsilon$. Thus the

probable error for any abscissa value ε is obtained immediately by merely substituting $x - \varepsilon$ for x in the well-known equation for r_a (*).

Using this simple equation I calculated in 1932 [4] the probable errors of the various combinations of universal constants represented by the various points on the Birge-Bond diagram, and indicated these uncertainties graphically by curves on each side of the straight line. This was done for a number of least squares solutions, corresponding to the use of various selected sets of experimental points, in order to discover if possible the most reliable result.

The simplification of the general Gauss equation just described applies *only* to the case of *two* independent variables, such as may be represented graphically by the Birge-Bond diagram. When three or more independent variables are assumed, the general equation *must* be used. In recent work by DUMOND and co-workers [60], at first five and later four independent variables (α , e , N and A) have been chosen. The very tedious work involved in repeated least squares solutions, using varying sets of experimental material, has been enormously accelerated by the use of an electronic digital computer. These investigations will be described in detail by Professor DUMOND and Dr. COHEN, in the papers to follow.

In closing this last section of my paper I should like to give a striking illustration of the extremely indirect processes that may now be employed to get highly precise calculated values of certain universal constants. In this calculation, which I carried out in 1950, it is the Rydberg constant, R_∞ , as calculated by the Bohr formula [61]. This paper was my last in the field, prior to the present summary address.

In place of the constants e , m , and h , which appear explicitly in Bohr's original equation, the new calculation involves, in addition to the Avogadro number, four experimentally determined quantities, all first obtained with high precision in the year or so preceding my paper. It involves also certain correcting factors whose uncertainties are less than those of the five main quantities. The four new quantities are: (1) γ_p , the gyromagnetic ratio of the proton [62]; (2) μ_p , the magnetic moment of the proton in terms of the Bohr magneton [63]; (3) the ratio ω_p^c/ω_e^c , where ω_p^c is the proton frequency corresponding to ω_e^c for the electron, which in turn represents the *orbital* re-

(*) We have

$$r_a = 0.6745 \left[\frac{(\sum p v^2)(\sum p x^2)}{(n-2)D} \right]^{\frac{1}{2}},$$

where

$$D = (\sum p x^2) - (\sum p)(\sum p x)^2.$$

The value of D is invariant to such a linear transformation and hence need not be recalculated [59].

sonance frequency of the electron in the magnetic field of the cyclotron, while ω_p represents the *nuclear precession* frequency of the proton in the same magnetic field [64]; (4) $\Delta\nu_H$, the hyperfine splitting of the $^2S_{\frac{1}{2}}$ level of hydrogen [65].

The calculated value, as thus obtained, is $R_\infty = (109733.61 \pm 7.03) \text{ cm}^{-1}$, a discrepancy with the very accurate spectroscopic value of only $(-3.69 \pm 7.03) \text{ cm}^{-1}$, or only 3.4 parts in 10^5 (and probable error of 6.4 parts). If one now uses the latest values, and latest probable errors, of all relevant quantities, the discrepancy is reduced to only $(-0.74 \pm 3.20) \text{ cm}^{-1}$, or to *less than one* part in 10^5 , with a probable error of *three* parts in 10^5 . This seems to me a truly remarkable verification of the Bohr formula.

One can now *assume* the correctness of the formula, in the form just considered, and use it to *calculate* a value of N . If this had been done in 1950 I would have obtained 6.02553 ± 0.00094 , in contrast with the observed value 6.02502 actually employed. With the use of all latest values one gets 6.02512 ± 0.00037 , in excellent agreement with the latest crystal value and the DuMond and Cohen calculated value already discussed in Sect. 5. It is one of the possible indirect values of N , many of which were considered by DuMond and Cohen in 1954 [44], and it has roughly the same probable error as the crystal value.

* * *

For a number of years preceding my retirement in 1955, I was so involved in administrative work that research was almost entirely neglected. Moreover, the increasing involvement of the calculations of the universal constants with the very complex developments of modern physical theory, with which I am not particularly familiar, made it difficult for me to continue effective work in the field. Because of these circumstances the scientific world should feel deeply indebted to Professor DuMond for the great amount of time and energy he and his coworkers, in particular Dr. COHEN, have been willing to devote to this rather unique field during the past decade or more.

As a result of Dr. DuMond's thorough knowledge of experimental techniques and Dr. COHEN's special knowledge of numerical mathematics, the critical evaluation of the universal constants, especially the atomic constants, has been kept up to date in a most admirable way. It is therefore with an entirely clear conscience that I have retired from a field that, unfortunately, has often involved delicate personal relationships quite as much as it has objective science. But it is also a field that furnishes an almost unique opportunity to make an acid test of the claimed objectivity of scientific research.

With an earnest plea that every one of us shall always remember that the revealing of scientific truth is the sole legitimate objective of scientific research, I close this very fragmentary and disconnected discourse.

REFERENCES

- [1] R. T. BIRGE: *Reports on Progress in Physics*, **8**, 90 (1941); to be denoted G.C. 1941
- [2] R. T. BIRGE: *Rev. Mod. Phys.*, **1**, 1 (1929); to be denoted G.C. 1929.
- [3] R. T. BIRGE: *Phys. Rev.*, **40**, 207 (1932); to be denoted L.S.1932.
- [4] R. T. BIRGE: *Phys. Rev.*, **40**, 228 (1932); to be denoted G.C. 1932.
- [5] R. A. MILLIKAN: *Phil. Mag.*, (6) **34**, 1 (1917). A detailed account of all his oil-drop work appears on pp. 88-122 of his book, *The Electron* (Chicago, 1917).
- [6] R. T. BIRGE: *Amer. Journ. Phys.*, **13**, 63 (1945). To be denoted G.C. 1945.
- [7] V. D. HOPPER and T. H. LABY: *Proc. Roy. Soc.*, A **178**, 243 (1941); E. BÄCHLIN and H. FLEMBERG: *Nature*, **137**, 655 (1936); Y. ISHIDA, I. FUKUSHIMA and T. SUETSUGU: *Sci. Papers, Inst. Phys. and Chem. Res. Tokyo*, **32**, 57 (1937).
- [8] E. L. HARRINGTON: *Phys. Rev.*, **8**, 738 (1916).
- [9] Pp. 92-93 of *The Electron* (ref. [5]).
- [10] J. A. BEARDEN: *Phys. Rev.*, **56**, 1023 (1939). This is one of the six new determinations already mentioned.
- [11] R. T. BIRGE: G.C. 1929 (ref. [2]), pp. 14-18. The figures given here are those used in 1929, namely $q = 0.99995$ for the coulomb, and $pq = 1.00046$ for the volt. The latest figures, as adopted by international agreement (*Science*, **105**, 40 (1947)), are $q = 0.99985$ and $pq = 1.00034$.
- [12] H. GEIGER and K. SCHEEL: *Handbuch der Physik* (Berlin, 1926), Vol.2, p. 503.
- [13] R. T. BIRGE: G.C. 1929, (ref. [2]), p. 38.
- [14] R. A. MILLIKAN: *Phys. Rev.*, (2) **7**, 355 (1916).
- [15] R. T. BIRGE: G.C. 1929 (ref. [2]), p. 50.
- [16] One of the relatively few correct diagrams is that by R. LADENBURG in W. WIEN and F. HARMS: *Handbuch der Experimentalphysik*, (Leipzig, 1928), Vol. 18, p. 3, see p. 13.
- [17] A. A. MICHELSON: *Astron. Papers of Amer. Ephemeris*, **1**, 109 (1882); see p. 117.
- [18] G. WOLFSOHN in H. GEIGER and K. SCHEEL: *Handbuch der Physik*, (Berlin, 1928), Vol. 19, p. 905
- [19] N. E. DORSEY: *Trans. Amer. Phil. Soc.*, **34**, 1 (1944).
- [20] A. A. MICHELSON, F. G. PEASE and F. PEARSON: *Astrophys. Journ.*, **82**, 26 (1935).
- [21] E. BERGSTRAND: *Ark. f. Fys.*, **2**, 119 (1950), see, p. 139.
- [22] R. T. BIRGE: *Nature*, **134**, 771 (1934).
- [23] W. C. ANDERSON: *Rev. Sci. Instr.*, **8**, 239 (1937), and *Journ. Opt. Soc. Amer.*, **31**, 187 (1941).
- [24] A. HÜTTEL: *Ann. d. Phys.*, **37**, 365 (1940).
- [25] E. B. ROSA and N. E. DORSEY: *U. S. Bur. Stand. Bull.*, **3**, 433 (1907).
- [26] E. BERGSTRAND: *Ark. f. Fys.*, **2**, 119 (1950); **3**, 479 (1951).
- [27] R. T. BIRGE: G.C. 1941 (ref. [1]), p. 132 for all references.
- [28] R. C. A. EDGE: *Nature*, **177**, 618 (1956).
- [29] A. A. MICHELSON: *Astrophys. Journ.*, **65**, 1 (1927).
- [30] LORD RAYLEIGH: *Nature*, **21**, 382 (1881) and **25**, 52 (1881).
- [31] W. C. ANDERSON: *Journ. Opt. Soc. Amer.*, **31**, 187 (1941). See p. 195.
- [32] A. A. MICHELSON: *Astron. Papers Amer. Ephemeris*, II, 231 (1891).
- [33] J. W. G. [GIBBS]: *Amer. Journ. Science*, **31**, 62 (1886).
- [34] H. BOUASSE: *Propagation de la Lumière* (Paris, 1925) p. 41.

- [35] C. GUTTON: *Compt. Rend.*, **152**, 1089 (1911).
- [36] R. LADENBURG in W. WIEN and F. HARMS: *Handbuch der Experimentalphysik* (Leipzig, 1928), Vol. **18**, 30.
- [37] J. LOSCHMIDT: *Wiener Ber.*, **52** II, 395 (1865). See also E. HOPPE in H. GEIGER and K. SCHEEL: *Handbuch der Physik* **1**, p. 128.
- [38] S. E. VIRGO: *Science Progress*, **27**, 634 (1933).
- [39] F. TYRÉN: *Nova Acta Reg. Soc. Sci. Uppsala* (IV), **12**, No. 1 (1940).
- [40] F. TYRÉN: *Zeits. f. Phys.*, **109**, 722 (1938).
- [41] See *Nature*, **155**, 643 (1945).
- [42] See *Journ. Sci. Instr.*, **24**, 27 (1947), *Phys. Rev.*, **72**, 436 (1947), *Acta Cryst.*, **1**, 46 (1948).
- [43] G. BROGREN: *Ark. f. Fys.*, **7**, 47 (1953).
- [44] J. W. M. DUMOND and E. R. COHEN: *Phys. Rev.*, **94**, 1790 (1954).
- [45] E. R. COHEN: *Phys. Rev.*, **101**, 1641 (1956).
- [46] M. E. STRAUMANIS: *Phys. Rev.*, **95**, 566 (1954). See also *Phys. Rev.*, **92**, 115 (1953) and *Zeits. f. Phys.*, **126**, 49 (1949).
- [47] A. S. EDDINGTON: *Proc. Roy. Soc.*, A **122**, 358 (1929).
- [48] Immediately, by private correspondence; later, *Nature*, **123**, 318 (1929).
- [49] A. S. EDDINGTON: *Proc. Roy. Soc.*, A **126**, 696 (1930).
- [50] R. T. BIRGE: G.C. 1929 (ref. [2]), p. 63.
- [51] R. T. BIRGE: G.C. 1941 (ref. [1]), p. 130.
- [52] A. S. EDDINGTON: *Proc. Phys. Soc.*, **45**, 271 (1933).
- [53] N. BOHR: *Phil. Mag.*, **26**, 1 (1913).
- [54] W. N. BOND: *Phil. Mag.*, **10**, 994 (1930) and **12**, 632 (1931).
- [55] R. T. BIRGE: G.C. 1932 (ref. [4]).
- [56] K. F. GAUSS: *Theoria combinationis etc.*, in *Werke*, Band IV, Section 29, pp. 34-35. See WHITTAKER and ROBINSON: *Calculus of Observations*, pp. 242-243, for a brief derivation.
- [57] H. SCHULTZ: *Journ. Amer. Statistical Ass.* **25**, 139 (1930).
- [58] R. T. BIRGE: L.S. 1932 (ref. [3]), pp. 225-226.
- [59] R. T. BIRGE: G.C. 1929 (ref. [2]), p. 5 and L.S. 1932 (ref. [3]), p. 226. See also *Amer. Journ. Phys.*, **7**, 351 (1939), Eqs. (37) to (42).
- [60] J. W. M. DUMOND and E. R. COHEN: *Rev. Mod. Phys.*, **25**, 691 (1953); E. R. COHEN, J. W. M. DUMOND, T. W. LAYTON and J. S. ROLLETT: *Rev. Mod. Phys.*, **27**, 363 (1955). See also references [47] and [48].
- [61] R. T. BIRGE: *Phys. Rev.*, **79**, 193 (1950).
- [62] H. A. THOMAS, R. L. DRISCOLL and J. A. HIPPLE: *Phys. Rev.*, **75**, 902 (1949).
- [63] J. H. GARDNER and E. M. PURCELL: *Phys. Rev.*, **76**, 1262 (1949).
- [64] J. A. HIPPLE, H. SOMMER and H. A. THOMAS: *Phys. Rev.*, **76**, 1877 (1949).
- [65] J. E. NAFF and E. B. NELSON: *Phys. Rev.*, **73**, 718 (1948).

Present Sources of Precise Information on the Universal Physical Constants.

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The experimental data of Table I upon which Dr. COHEN and I have based our latest set of values for the universal physical constants fall into two groups. In the group I shall discuss first, seven precisely measured experimental data which are so interrelated that they overdetermine four primary unknowns. This situation requires us to arrive at the output results by a least squares adjustment.

The auxiliary constants, which constitute the second group, on the other hand, are quantities so precisely known relative to the accuracy of the measurements of the first group, and are involved with the latter in the least squares adjustment in such a fashion, that nothing is gained by treating them as adjustable unknowns. Their measured values are therefore not subject to adjustment and are treated as though they were exactly known constants.

The four primary unknowns which we have selected for the least-squares adjustment are the Sommerfeld fine structure constant, α ; the electronic charge, e ; the Avogadro number, N , and the conversion constant, $A = \lambda_0/\lambda_s$, relating the two scales of wavelength, in angstroms on the one hand and in kilo X-units (SIEGBAHN) on the other.

Seven different functions of these four unknowns have been measured by experimental methods which we feel are sufficiently precise and reliable to qualify them as input data in a least squares adjustment. These seven experimentally determined numerical values are not only functions of the unknowns, α , e , N , and A , but also of the above mentioned experimentally determined auxiliary constants, of which last I shall mention five different kinds.

One of these auxiliary constants I find it expedient to recall to your attention at the very beginning to avoid any possibility of confusion. This is the conversion factor, r , between the «physical» and «chemical» scales of atomic weight.

TABLE I. — *Resumé of experimental data for determining the universal physical constants.*

Four primary unknowns whose least squares adjusted values are sought.			
$\alpha = 2\pi e^2/hc$	Sommerfeld's fine structure constant		
e	Electronic charge (expressed in abs. esu)		
N	Avogadro number (expressed in mole ⁻¹ , (physical scale))		
$A = \lambda_g/\lambda_s$	Conversion factor from X-units (SIEGBAHN) to mÅ		
First group (Least squares adjustment)			
Seven kinds of experimental data bearing on above unknowns			
No.	Function measured numeric	Estimated precision	Description of experiment
1.	$\frac{Ne}{c} \left\{ \begin{array}{l} = 9652.15 \\ = 9651.29 \end{array} \right.$	$\left\{ \begin{array}{l} (13 \text{ ppm}) \\ (20 \text{ ppm}) \end{array} \right.$	$\left. \begin{array}{l} \text{Iodine faraday} \\ \text{Silver faraday} \end{array} \right\}$ by electrochemistry
2.	$A = 1.002020$	(30 ppm)	X-Ray lines measured with ruled gratings
3.	$NA^3 = 0.606179 \cdot 10^{24}$	(38 ppm)	Crystal densities and grating constants in X-units
4.	$\frac{\alpha^3 c}{e} = 2.425517 \cdot 10^{13}$	(23 ppm)	Proton gyromag. ratio (THOMAS, DRISCOLL and HIPPLE)
5.	$\left\{ \begin{array}{l} = 3.979879 \cdot 10^{-10} \\ = 3.979423 \cdot 10^{-10} \\ = 3.979359 \cdot 10^{-10} \\ = 3.979444 \cdot 10^{-10} \end{array} \right.$	$\left\{ \begin{array}{l} (36 \text{ ppm}) \\ (11 \text{ ppm}) \\ (14 \text{ ppm}) \\ (36 \text{ ppm}) \end{array} \right.$	$\left\{ \begin{array}{l} \text{BLOCH and JEFFRIES: Inverse cyclotron} \\ \text{SOMMER, THOMAS and HIPPLE: Omegatron} \\ \text{COLLINGTON, DELLIS, SANDERS and TURBERFIELD} \\ \text{TRIGGER's correction to BLOCH and JEFFRIES} \end{array} \right.$
			Proton mag. mom. in nuclear magnetons by measuring ω_c/ω_p
6.	$\alpha^2 c = 1.596412 \cdot 10^6$	(9 ppm)	Microwave determination of fine structure splitting in deuterium
7.	$\left\{ \begin{array}{l} = 1968.750 \\ = 1968.911 \\ = 1968.869 \end{array} \right.$	$\left\{ \begin{array}{l} (51 \text{ ppm}) \\ (40 \text{ ppm}) \\ (83 \text{ ppm}) \end{array} \right.$	$\left\{ \begin{array}{l} \text{W. LAMB jr. and coworkers} \\ \text{Short wave-length limit of continuous X-ray spectrum} \end{array} \right.$
Second group (Regarded as fixed constants)			
Constants		Estimated precision	Kind
$H = 1.008142 \pm 0.000003$		(3 ppm)	$\left\{ \begin{array}{l} \text{Atomic weights (physical scale)} \\ \text{by method of nuclear reaction energies} \end{array} \right.$
$H/M_p = 1.00054461$			
$D = 2.014735 \pm 0.000006$		(3 ppm)	
$D/M_d = 1.00027244$			
$R_\infty = (109737.309 \pm 0.012) \text{ cm}^{-1}$		(0.11 ppm):	Rydberg constant by spectroscopic determinations
$\mu_e/\mu_p' = 658.2288 \pm 0.0004$		(0.6 ppm)	Ratio electron magnetic moment to proton magnetic moment
$\mu_n/\mu_0 = 1.00114536$		(<0.01 ppm)	Ratio electron magnetic moment to Bohr magneton
$c = (299793.0 \pm 0.3) \text{ km s}^{-1}$		(1 ppm)	Velocity of light

1. The chemical and physical scales of atomic weights.

The older of these two, the chemical scale, had its origin before the existence of isotopes was known. On the chemical scale the mean atomic weight of a mixture of the three isotopes of oxygen, ^{16}O , ^{17}O , and ^{18}O « in their naturally occurring abundance ratios » is defined as having atomic weight 16.0000. On the physical scale the atomic weight of the ^{16}O isotope has, by definition the atomic weight exactly 16. Atomic weights on the physical scale are numerically slightly the larger.

On the basis of the following assumed isotopic abundance ratio

$$(1) \quad ^{16}\text{O} : ^{18}\text{O} : ^{17}\text{O} = (506 \pm 10) : 1 : (0.204 \pm 0.008)$$

and the masses $^{16}\text{O} = 16.0000$ (by definition), $^{18}\text{O} = 18.0049$, $^{17}\text{O} = 17.0045$ BIRGE [1] has computed the conversion factor, r , between the chemical and physical scales of atomic weight as

$$(2) \quad r = 1.000272 \pm 0.000005 \quad (\text{BIRGE, 1941}).$$

However the definition of the chemical scale of atomic weights is an equivocal one because there is no exactly defined « naturally occurring abundance ratio » of the oxygen isotopes. A. O. NIER in a study [2] of the relative abundance of isotopes would revise BIRGE's values of r *upward* about 6 parts per million, if the abundance ratio for atmospheric oxygen is taken as defining the chemical scale of atomic weights. NIER says that oxygen from limestone would agree with this but if oxygen from iron ore or water were employed, the ^{18}O content might be 4 percent lower and the conversion factor, r , would be only about 1.000268, some 4 ppm *lower* than that chosen by BIRGE. Eventually the chemical scale will probably be defined by a conventionally adopted value of r (*).

Because of the unequivocal nature of its definition and because extremely accurate atomic weights can be derived in terms of it from measurements of nuclear reaction energies, we shall here base our calculations on the *physical* scale of atomic weights.

(*) In a private communication from E. WICHERS of the U. S. National Bureau of Standards we are informed that the International Commission on Atomic Weights has been considering redefinition of the chemical scale of atomic weights. The definition most probably will be based on the use of the exact number, 16, as the atomic weight of a mixture of the natural isotopes of oxygen whose average atomic mass is greater by an exact factor (probably 1.000275) than the mass of ^{16}O . The difference of 3 ppm between this value of the conversion factor and that of Birge which we have used in the adjustment we are here describing makes no significant change in any of our output results.

PART I

INPUT DATA FOR LEAST SQUARES ADJUSTMENT

2. - Faraday constant by electrochemical methods.

The silver [3] and the iodine [4, 5] coulometers are the two instruments for measuring the faraday which have received the most study. The experimental work was done in both cases prior to 1916. A study of the work on the silver voltameter clearly shows that the emphasis at that time was directed towards obtaining *reproducible* values of the electrochemical equivalent rather than a measurement of absolute fundamental significance for the purpose of determining the faraday. This was natural since the objective at the time was to obtain specifications for a working procedure which would empirically define the ampere with as much reproducibility as possible. Three possible sources of error in the use of the silver voltameter for an absolute precision determination of the faraday can be cited. (i) The measured gain in weight of the cathode may not be entirely due to deposited silver; there may be in the deposit «inclusions» of other matter from the electrolyte. (ii) Some of the deposited silver may redissolve in the electrolyte, or otherwise become detached, before weighing. (iii). The deposited silver may not have quite the same isotopic constitution as that of «natural» silver on which the accepted value of the chemical atomic weight of that element (the value used in computing the faraday) is based. When these voltameter experiments were performed isotopes had not yet been discovered, and the atomic weight of a naturally occurring element such as silver was thought to be an invariable quantity. It is now known that electrolysis may well introduce an appreciable change in isotopic constitution and thereby affect the mean atomic weight. Silver has two isotopes of almost equal abundance which differ in mass by about 2 percent. This abundance ratio is the most favorable one for producing a systematic error through selective electrolytic separation. If in the cathode deposit the ratio of the light to the heavy isotope content is greater by 1 percent than it is in the solution, the deposit will be 46 ppm lighter than if no such selective separation had occurred.

Iodine, on the other hand, occurs naturally in only one stable isotopic form, ^{127}I , and it is possibly significant that the electrolytic faraday determination of G. W. VINAL and S. J. BATES [4, 5] made with the «iodine coulometer» disagree with those of the silver voltameter by an amount considerably greater than the obvious experimental estimates of uncertainty would lead

one to expect. Not only is this true but the iodine results are in much better accord with the consensus of present data on the atomic constants than are the silver results.

In the iodine coulometer the reaction



takes place from left to right at the cathode and in the reverse sense at the anode. The changes in the amounts of «free iodine» at the two electrodes are determined by titration. Their equality (with opposite sign) furnishes an important check on the purity of the reaction. The iodine coulometer therefore contains within itself the proof of its own correctness (*).

The faraday values obtained by the two coulometers have recently been recalculated by G. W. VINAL (1949) and later (1951) corrected by J. A. HIPPLE

(*) This instrument was first developed by E. W. WASHBURN and further perfected by one of his students, S. J. BATES. In view of the great advantages of the iodine coulometer over the silver voltameter it is most surprising that this method was not adopted in place of the electrolysis of silver for standardizing and reproducing the coulomb and the ampere by the International Technical Committee in the early part of this century. These advantages, listed by S. J. BATES in his doctorate thesis, 1912 [4], were later fully substantiated by a study at the U. S. National Bureau of Standards done in 1914 by S. J. BATES and G. W. VINAL [5]. BATES in his thesis explains the working of the iodine coulometer as follows.

«An aqueous solution of potassium iodide to which iodine has been added contains both iodide and tri-iodide ions. When a current of electricity is passed through such a solution the reaction



takes place in the direction from left to right at the cathode and in the reverse direction at the anode. Hence a cell in which the electrodes are surrounded by such a solution should contain the same total amount of «free iodine» before and after the passage of an electric current. By separating the electrodes and the solutions surrounding them by a conducting solution of an iodide, the changes in the amounts of «free iodine» at the two electrodes can be determined by titration and if the reaction is a perfectly clean-cut one, free from all disturbing side reactions, the results at the two electrodes should check each other. The iodine coulometer therefore contains *within itself* the proof of its own correctness, for if it can be shown that identical amounts of iodine are involved in the reactions at *both* electrodes under varying conditions of concentration and current density it will establish beyond question the fact that *the only reaction*, involving electricity, which occurs at the anode is that expressed by the above equation. In this particular the iodine coulometer possesses an enormous advantage over the silver coulometer, for, as is well known, no such quantitative proof of the nature of the reaction is possible with the latter coulometer».

BATES in his thesis compared the results of eight runs with two iodine coulometers in series and obtained an average deviation from the mean of each pair of results of only 20 ppm.

for the new atomic mass of iodine with the following results:

$$(4) \quad \text{Iodine faraday} = Ne' = \\ - (9652.15 \pm 0.13) \text{ abs emu (g equiv)}^{-1} \text{ (physical scale),}$$

$$(5) \quad \text{Silver faraday} = Ne' = \\ = (9651.29 \pm 0.19) \text{ abs emu (g equiv)}^{-1} \text{ (physical scale).}$$

The difference between these two results, $(0.86 \pm 0.23) \text{ emu (g mole)}^{-1}$ (physical scale) is uncomfortably large in comparison to its expected standard error.

It was the effort to achieve better consistency in the entire picture of the determinations bearing on the atomic constants which first emphasized the above discrepancies (*) and indicated that the iodine value was more likely to be the true one.

Our most recent adjustment of the atomic constants still supports the view that the iodine value is more nearly correct than the silver values as Dr. COHEN's analysis will show. The true source of the discrepancy is still obscure however in spite of two further investigations (**) undertaken in an effort to clarify the matter.

(*) As early as 1929 R. T. BIRGE [6] distinguished a systematic difference between what he called the «spectroscopic» and the «deflection» values of e/m , the charge-to-mass ratio for the electron. He at first thought that e/m might be different depending on whether the electron was «inside» an atom or «in free space». In reality his so-called spectroscopic measurements of e/m amounted to determinations of the ratio of the electronic and nuclear masses (by comparison of the Rydberg value for different light atoms) and a value of the faraday constant had to be introduced to compute e/m from the spectroscopic data. This constant, did not enter in deriving e/m from «deflection» measurements, however. BIRGE initially had preferred the silver value to the iodine value because of the great care which had been expended to make the method highly reproducible and partly because it was then regarded as the basis for defining the international coulomb. DuMOND first pointed out (in 1940) that the apparent difference between the two sets of values of e/m might stem from a systematic error in the silver faraday value, a suggestion which Prof. BIRGE [7] immediately accepted as plausible.

(**) One of these was by A. F. SCOTT of Reed College, Portland, Oregon [8] and the other by D. N. CRAIG and J. I. HOFFMAN at the U. S. National Bureau of Standards [9]. The first of these comprised a careful review of all methods to determine the amount of «inclusions» in the silver deposit of the silver coulometer and an attempt to estimate inclusions by means of radioactive tracers. The second was a redetermination of the faraday with a coulometer employing the electrolytic oxidation of sodium oxalate in a supporting solution of sulphuric acid. The reaction,



was carried out in a coulometer with a gold anode and a platinum cathode, the anode and cathode vessels being connected electrically through four siphons dipping into

Further work on the iodine coulometer is reported to be in progress at the Rockefeller Institute for Medical Research, New York, N.Y., by D. A. MAC INNES [10] using several improvements depending on newly developed modern techniques.

The high faraday value obtained with the iodine coulometer has received support also from a direct measurement of the charge-to-mass ratio for protons of which I shall speak presently.

3. - The conversion factor, $A = \lambda_g/\lambda_s$, from Siegbahn X-units to milliangstroms.

The wavelengths of X-ray spectral lines measured relative to each other by the high precision methods of crystal diffraction are known with a precision of one part in 10^4 to 10^5 . This precision exploration and tabulation of the X-ray spectrum was first brought to high perfection by M. SIEGBAHN [11] and his school. Later, with such improvements as the two-crystal spectrometer and the curved crystal spectrometer, it was carried even further by many others [12, 13]. About 3000 of these precision wavelength measurements have been tabulated [14] and they constitute a very reproducible and

three beakers to isolate anode and cathode solutions. A weighed quantity of sodium oxalate was added to the anode vessel and, after the electrolytic oxidation, the residual oxalate was determined by titration with KMnO_4 . As CRAIG and HOFFMAN point out, the oxalate coulometer has the advantage that since a large fraction by weight of the measured substance, C_2O_4 , is oxygen, the errors resulting from uncertainties in atomic weight are minimized.

Seventeen determinations of the faraday, twelve with a small and five with a large oxalate coulometer were made with results ranging from about 9652.6 to 9651.1 absolute emu per gram equivalent on the physical scale of atomic weights. The mean of their oxalate values came out lower than the iodine faraday. The difference,

$$(0.8 \pm 0.32) \text{ abs emu (g equiv)}^{-1},$$

is still uncomfortably large relative to its expected standard deviation. The difference between the mean of the oxalate values and the silver value on the other hand is

$$(0.06 \pm 0.36) \text{ abs emu (g equiv)}^{-1}.$$

"This very good agreement could indeed be considered as a verification of the silver value if no other information were available. Actually however a study of the sequence of results obtained in seventeen measurements by the oxalate method shows a decidedly marked trend downward when the results are arranged in the temporal order in which the measurements were performed. The first two measurements are in good accord with the weighted mean of the iodine values whereas the mean of the last two measurements yields a value more than 1 absolute emu lower. This downward trend shows no suggestion of levelling off in the plot presented in CRAIG and HOFFMAN's paper. Such behavior strongly suggests an experiment «out of control». The reason is obscure but the suspicion is inescapable.

well defined natural scale of lengths in the range between about 10^{-9} and $4 \cdot 10^{-6}$ cm. To express these wavelengths in centimeters or Angstrom units the method first adopted was that of Sir. WILLIAM BRAGG [15] in which the Avogadro number was taken as the quotient of the faraday by Millikan's oil drop value of e . From the Avogadro number and the atomic weights of its constituents the absolute weight in grams of the unit cell of a crystal could be computed and this together with the macroscopic density and geometry of the crystal permitted calculation of its grating constant. As the result of precision work by COMPTON, BEETS, and DEFOE [16] on calcite M. SIEGBAHN adopted as the basis for calculating X-ray wavelengths the «effective» (*) grating space of calcite at 18 °C in first order reflection at the conventional value

$$(6) \quad d''_{18} = 3\,029.040 \text{ X-units}.$$

SIEGBAHN's intention was that the X-unit should be one milliangstrom. He very wisely, however, chose to call this unit of length by a distinctive name, no doubt because he realized that its absolute value might some day require revision. We now know that Millikan's oil drop value of e was erroneous chiefly because of the erroneous value of the viscosity of air which entered his computations and this error was propagated into the calculations which led to the calcite grating space. For this reason it is best to regard Siegbahn's system of wavelengths in X-units as a purely arbitrary unit system.

The discrepancy between Siegbahn's X-unit and the milliangstrom was first noted by E. BÄCKLIN [17], I believe, when the wavelengths of certain soft X-ray lines, which had been measured in X-units by the methods of crystal diffraction, were also precisely measured with artificially ruled gratings calibrated as to grating constant with optically known wavelengths.

Save for the case of extremely long X-ray wavelengths, the great bulk of the ruled grating measurements of X-ray lines have been made using plane gratings in grazing incidence. COMPTON and DOAN [18] and shortly afterward THIBAUD [19] were the first to use this method. Fig. 1 of the Table II illustrates the geometry for the case of grazing incidence and compares the

(*) The «effective» grating space, d_n , includes a certain correction term for refractive index and is not strictly a constant but a function of the order of interference in Bragg reflection. For the calcite cleavage planes, for example, d_n is related to the true grating space, d , by the equation,

$$d_n = d[1 - 135 \cdot 10^{-6}/n^2],$$

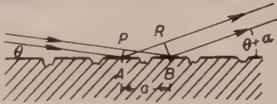
and the corrected Bragg equation is written

$$n\lambda = 2d_n \sin \theta_n.$$

dispersions obtainable in grazing and in normal incidence. A condition for sufficient intensity in the diffracted spectrum is that the angle of grazing incidence shall be less than the critical angle for total reflection of the X-rays.

TABLE. II - Conversion factor, $\Lambda = \lambda_g/\lambda_s$, from X-units to mÅ.

Ruled gratings calibrated with optical light are used at grazing incidence to measure X-ray line wavelengths.



Path difference:

$$PB - AR = a[\cos \theta - \cos (\theta + \alpha)] = n\lambda.$$

In the simplest case of completely grazing incidence we have:

$$\theta \rightarrow 0 \quad \text{and} \quad n\lambda = a(1 - \cos \alpha) = \alpha^2/2.$$

Dispersion for normal and for grazing incidence compared.

Grazing Incidence:

$$(d\alpha/d\lambda)_g = \sqrt{n/2a\lambda},$$

If $\lambda = 1\text{\AA}$, $a = 10^{-4}\text{ cm}$ and $n = 1$,

$$(d\alpha/d\lambda)_g = 0.4 \cdot 10^{-2} \text{ rad/\AA}$$

Normal Incidence:

$$(d\alpha/d\lambda)_n \simeq n/a \text{ (for small } \alpha)$$

If $a = 10^{-4}\text{ cm}$ and $n = 1$

$$(d\alpha/d\lambda)_n = 10^4 \text{ rad/\AA}$$

The outstanding experimental work on the comparison of grating and SIEGBAHN wavelengths of X-ray lines has been done by J. A. BEARDEN [20], E. BÄCKLIN [21], M. SÖDERMANN [22], and by F. TYRÉN [23].

TABLE III. - E. T. Birge's comparison of grating and Siegbahn wavelengths of X-rays (1945).

Author	X-Ray Line	Value of $(\Lambda - 1) \cdot 10^6$ (P.E. based on accidental errors only)	Birge's adopted P.E.
BEARDEN	CuK $\alpha_{1,2}$	1980 \pm 31	\pm 52
BEARDEN	CuK $\beta_{1,3}$	2079 \pm 28	\pm 50
BEARDEN	CrK $\alpha_{1,2}$	2036 \pm 21	\pm 48
BEARDEN	CrK $\beta_{1,3}$	2017 \pm 28	\pm 48
SÖDERMAN	AlK $\alpha_{1,2}$	2070 \pm 37	\pm 84
BÄCKLIN	AlK $\alpha_{1,2}$	2000 \pm 14	\pm 60
BEARDEN	CuK $\alpha_{1,2}$	2087 \pm 55	\pm 130
TYRÉN	AlK $\alpha_{1,2}$	2024 \pm 5	\pm 48

BIRGE's 1945 adopted average: $\Lambda = 1.002\,030 \pm 0.000\,020$.

Sir LAWRENCE BRAGG (1947) after consultation with SIEGBAHN, WARREN and LIPSON, with due consideration given to the above data listed by BIRGE, recommended for general adoption: $\Lambda = 1.002\,020 \pm 0.000\,030$.

The results have been summarized by R. T. BIRGE [24] in 1945 and are shown on the accompanying Table III together with the weighted average value of the conversion factor, A , which he adopted at that time:

$$(7) \quad A = 1.002\,030 \pm 0.000\,020.$$

In 1947 however Sir LAWRENCE BRAGG, after consultation with M. SIEGBAHN, B. E. WARREN and H. LIPSON, and with due consideration given to the above data listed by BIRGE, recommended for general adoption

$$(8) \quad A = 1.002\,020 \pm 0.000\,030.$$

[*Note added July 19, 1956.*]

The chief argument for this revision downward in 1947 was based on the work of F. TYRÉN in his dissertation (Uppsala 1940).

In this work by means of a concave grating vacuum spectrometer TYRÉN had carefully compared on the same plates the wavelength positions of four X-ray lines with the wavelength positions of several Lyman series spark lines emitted by highly ionized one-electron atoms. The wavelengths of these calibration lines he *calculated* using formulae based on the Sommerfeld-Dirac theory. At that time that theory was considered to give a rigorously accurate description of the one-electron atom. In 1950 however the discovery, by W. LAMB Jr. and R. C. RETHERFORD, changed all this and we now know that the formula used by TYRÉN to compute the wavelengths of his calibration lines requires a correction for the «Lamb shift» varying from 100 ppm for his ^{VIII}O Lyman alpha line to about 27 ppm for his ^{IV}Be Lyman delta line. The following Table IV gives the relative amount, in parts per million, by which the calibration wavelengths used by TYRÉN must be increased to correct them for the Lamb shift.

TABLE IV.

Line	^{VIII}O	^{VII}N	^{VI}C	VB	^{IV}Be
Lyman alpha	98.5	81.5	64.5	49.0	34.5
Lyman beta	84.0	69.0	54.7	41.0	29.0
Lyman gamma	79.0	65.5	52.0	39.1	27.5
Lyman delta	77.5	63.5	50.4	38.3	26.8

I must confess that I only awoke to the need for this correction about four days before the scheduled date of my departure from California for my present trip to Europe. To my knowledge the need for this correction has never before been cited in any published work. Unfortunately the dissertation of TYRÉN does not give the precise way in which his different calibration lines

were associated in their different orders of reflection with his different X-ray lines, so that it is impossible to give more than a rough estimate of what change the Lamb shift produces in TYRÉN's published results. My colleague, E. R. COHEN, has made such an estimate based on the assumption that each X-ray line was associated in every case with that calibration line most nearly adjacent to it in wavelength and he thus has arrived at a corrected weighted mean value of λ for TYRÉN's dissertation of

$$\lambda = 1.002\,026 \pm 0.000\,016 \quad (\text{TYRÉN corrected for Lamb shift}),$$

Tyrén's original uncorrected value, on the other hand had been

$$\lambda = 1.001\,99 \quad (\text{TYRÉN uncorrected for Lamb shift}).$$

Taking a similarly corrected value for BÄCKLIN's work of 1.002 03 and taking BEARDEN's work at the average value of 1.002 08, an equally weighted average of these three yields

$$\lambda = 1.002\,045 \quad (\text{Tentative estimated grand mean}).$$

I should like to emphasize that these are only tentative estimates and that the uncertainty as to how to correct TYRÉN's results makes it impossible at present to do more than place widely separated upper and lower bounds on the magnitude of the upward shift (between 27 ppm and 100 ppm).

It seems apparent however that the discrepancy between the American results on λ , as obtained by BEARDEN [25] without recourse to calculated calibration lines and the lower Swedish values is essentially to be explained in favor of the higher American values because of the need for the Lamb shift correction. The absolute measurements with plane gratings exhibit somewhat more random error however than the concave grating measurements and I should like to urge therefore that the method used by TYRÉN be reinvestigated in the light of our new knowledge.

A change in the input values of λ adopted for our least squares adjustment propagates its effect to greater or less extent into the least squares adjusted values of every constant and conversion factor we have calculated in our output tables. For example, an increase of one part per million in λ is estimated to produce a change Γ_{λ} in each of the constants of the following Table V which is given in parts per million by the accompanying numeric values.

TABLE V.

	e	m	h	α	λ	N	F	$hc^2/e\lambda$
Γ_{λ}	0.686	1.108	1.289	0.086	1.000	— 1.035	— 0.348	— 0.403

$hc^2/e\lambda$ is the voltage-wavelength conversion factor in kV X-units.

If the shift in λ turns out to be only 25 ppm (from 1.002 02 to 1.002 045) scarcely any of the constants and conversion factors given in our tables, with the possible exception of λ itself, will be shifted by as much as one whole standard deviation as therein tabulated. A change of 100 ppm would of course have much more serious consequences.

[*End of note added July 19, 1956.*]

4. — The Siegbahn-Avogadro number, $N_s = NA^3$. (By the X-ray-crystal-density method.)

The philosophy of the X-ray-crystal-density (XRCD) determinations of Avogadro's number, N , reverses the order of reasoning followed by SIEGBAHN which we have just previously sketched. If the length of one edge of the unit cell in a cubic crystal is denoted by d , and the density of the crystal by ρ , then $d^3\rho$ is the mass of the unit cell. If there are f molecules in a unit cell, and if M is the molecular weight, then $d^3\rho/f$ is the mass per molecule and Avogadro's number, N , the number of molecules in a gram mole, will be the ratio of these last two quantities, i.e., $N \Rightarrow Mf/\rho d^3$. M and N must of course be expressed on the same scale of atomic weights. For crystals in general, the volume of a unit cell is given by φd^3 where φ is a geometric factor (*).

The general formula for Avogadro's number computed in this way is then

$$(9) \quad N = Mf/\rho\varphi d^3.$$

The grating constant, d , is measured by means of X-rays, that is to say, by measuring the Bragg angle for critical reflection of some X-ray spectral line of known wavelength in X-units reflected by the atomic planes whose grating constant, d , is sought. As a result of the X-ray measurements, d will be expressed in X-units; if we use d_x to indicate that the crystal spacing is so expressed, we have:

$$(10) \quad N = mf/\rho\varphi d_x^3 A^3.$$

The quantity which the XRCD measurements really determine is therefore

$$(11) \quad N'_s = NA^3 = Mf/\rho\varphi d_x^3,$$

(*) For the calcite rhomb, φ is the volume of a rhombohedron whose three equal obtuse dihedral angles, α , have the value, $105^\circ 3' 5''$ and the distances between whose three parallel pairs of faces is unity. For this case J. A. BEARDEN [25] obtained

$$\varphi = 1.09594 \pm 0.00001.$$

for which we might coin the name, the Siegbahn-Avogadro number, since it is the result of computing Avogadro's number from the measured properties of a crystal whose grating constant, d , has been measured on the Siegbahn nominal scale of X-units.

R. T. BIRGE has reviewed [26] the entire question involving the determination of N from five different crystals—calcite, rock salt, diamond, lithium fluoride, and potassium chloride; see Table VI (*).

TABLE VI. Probable errors in parts per million for factors of N_s and the resulting values.

Crystal	Q_{20}	d_{20}^3	Resulting error in N_s	N_s (10^{23} mole $^{-1}$) (chemical scale)
Calcite	37	16.5	65	6.05989 ± 0.00039
NaCl	37	60	87	6.06077 ± 0.00052
Diamond	34	89	97	6.06018 ± 0.00059
LiF	45	120	132	6.05994 ± 0.00080
KCl	37	68	86	6.05999 ± 0.00052

Adopted weighted mean 6.06014 ± 0.00023

From these data the weighted mean value of N_s on the chemical scale of atomic weights is

$$(12) \quad N_s = NA^3 = (6.06014 \pm 0.00023) \cdot 10^{23} \text{ (g mole)}^{-1} \text{ (chemical scale)}.$$

We convert this to the physical scale using BIRGE's value of r :

$$(13) \quad N_s = NA^3 = (6.06179 \pm 0.00023) \cdot 10^{23} \text{ (g mole)}^{-1} \text{ (physical scale) (**)}.$$

5. - γ_p , the gyromagnetic ratio of the proton.

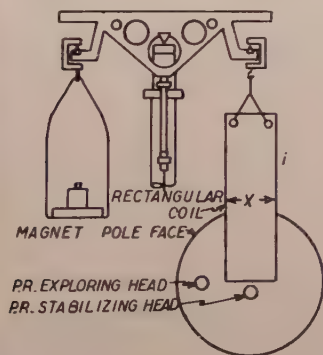
It is well known that atomic nuclei exhibit the properties of angular momentum (« spin ») and magnetic dipole moment, with the magnetic dipole

(*) Table VI gives an adaptation of Birge's conclusions. (The data are his in essence although we have taken the liberty to re-express them directly in terms of N_s).

(**) It would be premature to draw an inference at this point as to the « best » value of the Avogadro number, N , by combining this value of NA^3 with the previously measured value of A . Such an inference should only be drawn after the complete least squares adjustment has been made so that the value may be based on the *entirety* of our physical information.

axis along the axis of spin. When a proton is placed in a magnetic field, one may think, to use a classical picture, of a torque exerted on the proton dipoles which tends to align them with the field. In view of their spin, however, they respond to the externally applied torque by precessing around an axis parallel to the external field with a frequency of precession which is proportional to the applied external magnetic field (Table VII). The experiments at Harvard [27] and at Stanford [28] have shown that this «precession frequency» of the spinning protons can be measured very simply by placing a sample of water, sealed in a glass bulb, in a constant homogeneous magnetic field. A coil of wire, supplied with radio-frequency current and with its axis perpendicular to the magnetic field, surrounds this sample. When the magnetic field of the applied radio-frequency resonates with the precession frequency of the protons, an exchange of energy occurs and the resulting perturbation of the precessing protons causes them to induce a detectable «signal» either in the applied radio frequency coil itself (thereby changing its apparent impedance) or in a second detecting coil at right angles to the first. The Harvard method utilizes a single coil, the Stanford method two coils.

TABLE VII. - Measurement of γ'_p gyromagnetic ratio of the proton (before diamagnetic correction).



Field distribution between pole pieces of an electromagnet was first carefully explored with a proton resonance head. The field B_a was then measured in absolute units by weighing the force exerted on a rectangular current-carrying coil of accurately measured dimensions with its lower end suspended in the field [29].

The ratio, γ_p , between the proton precession frequency, ω_p , and the magnetic field intensity, B , is an extremely important constant or conversion factor because the method of proton resonance has proven itself to be by far the most convenient and accurate absolute method of measuring magnetic field intensities when these are in the range above a few hundred gauss.

In a hydrogen molecule the external applied magnetic field, B_a , differs slightly from the magnetic field, B , at the proton because of the diamagnetic effect of the electrons. The measured precession frequency, ω_p , the apparent gyromagnetic ratio, γ'_p (before diamagnetic correction), and the externally

applied field B_a are related by

$$\omega_p = \gamma'_p B_a.$$

N. RAMSEY [30] has computed the correction to the field for diamagnetism for the hydrogen molecule. He obtained: $-2.7 \cdot 10^{-6} B$.

The gyromagnetic ratio of the proton has been measured at the U.S. National Bureau of Standards by THOMAS, DRISCOLL and HIPPLE [29] with a precision of about 22 parts per million. In this experiment the field distribution between the pole pieces of an electromagnet was first carefully explored by means of a small proton resonance detector. The field was then measured by weighing the force exerted on a rectangular current-carrying coil of exactly measured dimensions whose lower end was suspended between the pole pieces. The result was

$$(14) \quad \gamma'_p = \omega_p/B_a = (2.67523 \pm 0.00006) \cdot 10^4 \text{ rad s}^{-1} \text{ gauss}^{-1}.$$

6. - ω_c/ω_p , Ratio of the cyclotron frequency of the proton to its magnetic resonance frequency: the proton magnetic moment in nuclear magnetons.

The term « cyclotron frequency of the proton » is related to the well known underlying principle of the simple magnetic resonance particle accelerator of E. O. LAWRENCE, the constant field, constant frequency cyclotron. A particle with charge-to-mass ratio, e/m , in a magnetic field of constant intensity, B , executes circular orbits with an angular frequency of rotation which, at non-relativistic speeds, is independent of the radius of the orbit. If the charge, e , is expressed in esu, this frequency is given by

$$(15) \quad \omega = Be/mc.$$

When the charged particle is a proton the angular resonance frequency so obtained is the « proton cyclotron frequency », ω_c , and if we measure B by the method just previously described in terms of the proton resonance frequency, ω_p , we obtain an important measure of the charge-to-mass ratio e/m_p of the proton, a datum of great interest for our knowledge of the atomic constants. Combining our equations for ω_c and ω_p (Eqs. (14) and (15)) one sees that the ratio, ω_c/ω_p , the cyclotron frequency of the proton to the proton magnetic resonance frequency is a universal constant

$$(16) \quad \omega_c/\omega_p = (e/m_p c) \gamma'_p{}^{-1},$$

whose reciprocal is, in fact, the apparent magnetic moment of the proton, μ' ,

(uncorrected for diamagnetism) (*) expressed in nuclear magnetons, $\mu_n = eh/4\pi m_p c$, where e is expressed in absolute esu and m_p is expressed in grams.

To determine ω_c , SOMMER, THOMAS, and HIPPLE [32] at the U. S. National Bureau of Standards built a miniature cyclotron which they called the «omegatron» because it determined the angular frequency, ω_c . In the omegatron the maximum orbit radius was only 1 cm. The high vacuum (10^{-7} mm Hg) in this small apparatus, shown schematically in Fig. 1, contained residual hydrogen, and ions (protons) were formed along an axis parallel to the magnetic field in the center of the device by impact from an axial beam of electrons. At right angles to the magnetic field a spatially uniform radiofrequency electric field (of variable frequency and of order 7 MHz) accelerated ions of a selected charge-to-mass ratio at their cyclotron resonance frequency in spiral orbits until they attained a radius of one centimetre, at which point they struck a collector. The resulting current was measured with an electrometer tube amplifier. An ion having a particular charge-to-mass ratio could attain a radius sufficient to reach the collector only when the frequency was tuned for ions of this type. The frequency width of the resonance peak so established depends on the number of orbital revolutions which the proton makes while it is being accelerated from zero radius out to the radius of the collector. It was possible to make this of the order of several thousand so that the resolution was extremely sharp. The magnet furnishing the field was the same one used in determining γ_p , and the cyclotron frequency of the proton was measured in relation to the nuclear resonance frequency of the proton. For this purpose the two resonance devices (cyclotron and nuclear) could be

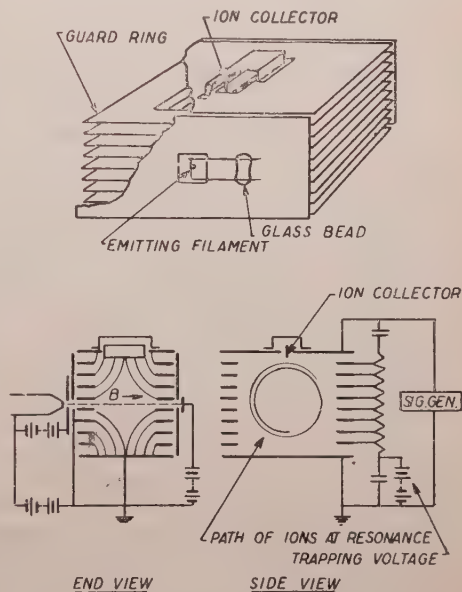


Fig. 1. — The «omegatron».

(*) If one desires to know the absolute magnetic moment of the proton, μ , the above mentioned small correction must be made for the fact that the magnetic field intensity at the proton is not exactly the same as the externally measured magnetic field, because of the diamagnetic effect of the proton-containing sample. The diamagnetic effect for hydrogen gas has, as we have said, been computed by N. F. RAMSEY [30] and the small additional shifts, of the order of a part in 10^6 , when water or mineral oil are used have been measured by H. A. THOMAS [31].

quickly interchanged while a third nuclear resonance probe, through a servo-system employing the probe signal, held the field constant (*).

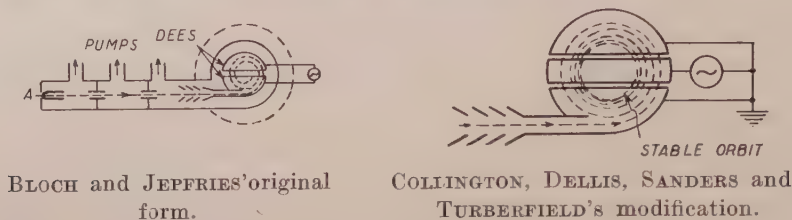


Fig. 2. - Two forms of the «inverse cyclotron».

F. BLOCH and C. D. JEFFRIES [33, 34] have also measured the cyclotron frequency of the proton by a method differing from that of the omegatron, in that the protons were injected at high speed (a kinetic energy of 20 000 electron volts) and were decelerated by cyclotron action. They therefore called their device an «inverse cyclotron» (Fig. 2). It differed from the omegatron also in that «dees» were provided so that the region in which the protons

(*) A small source of systematic error was carefully studied. This came from the presence of a D.C. electric field which had to be provided to stabilize the proton orbits against axial drift. There must clearly be, in addition to the component of this D.C. field in the axial direction, a component in the radial direction and this latter must exert forces and (unlike the magnetic field) do work on the spiralling protons. The force from this D.C. field is much smaller than the magnetic force but it depends on the radius, ϱ , in a way not very dissimilar from the latter. At the resonant frequency, $\omega_r = B(e/m_p c)$, the normal magnetic force on the proton is

$$F_{\text{mag}} = \frac{Be\omega_r}{c} \varrho,$$

while we may, to first approximation, express the radial component of the D.C. stabilizing field force as

$$F_{\text{el}} = -k\varrho.$$

Thus the frequency, ω_r , would be slightly shifted by this additional force. This effect was carefully studied by varying the magnitude of the electric stabilizing field over a considerable range and plotting a curve showing the slight variation of the apparent proton cyclotron frequency as a function of the D.C. stabilizing field. This curve turned out to be linear as expected and could be extrapolated to zero electric field so as to correct for the latter. However these experimenters found a still better way to make this correction. This depends on the fact that, whereas the resonance frequency, ω_r , is inversely proportional to the mass of the accelerated particle, the shift in frequency, $\Delta\omega$, due to the radial electric field, is independent of this mass. By determining in each case the resonant frequency for two different masses, e.g., H^+ and H_2^+ , and H^+ and D_2^+ , H^+ and H_2O^+ it was possible to evaluate the correction. After making this correction the average deviation from the mean was 1 part in 40 000, a result which gives considerable confidence in the reliability of the correction.

encountered the high frequency decelerating field constituted a very small fraction of a revolution. In consequence, it was possible to operate the device in « higher orders », that is to say at frequencies which were odd multiples of the frequency of revolution. Up to eleven half-cycles of the high frequency could occur during a half revolution of the particles, and much additional resolution was thus gained.

The respective results of the inverse cyclotron and the omegatron.

$$(17) \quad \mu' = 2.792365 \pm 0.000100 \text{ (36 ppm) (inverse cyclotron),}$$

$$(18) \quad \mu' = 2.792685 \pm 0.000030 \text{ (11 ppm) (omegatron),}$$

differ by only 115 parts per million, but the difference is uncomfortably large relative to the standard deviations assigned to each experimental result. The difference is in fact three times its root mean square expectation value. Work has since been published by COLLINGTON, DELLIS, SANDERS and TURBERFIELD [35] who repeated the inverse cyclotron experiment at the Clarendon Laboratory, Oxford. They did not use conventional cyclotron « dees ». Instead they had a central electrode with straight parallel sides to which the radio-frequency was applied while two grounded segmental electrodes on either side completed the cylindrical box. With this arrangement the protons were decelerated to such a radius that they eventually attained orbital stability without further gain or loss of energy.

The value of μ' (uncorrected for diamagnetism) obtained by COLLINGTON, DELLIS, SANDERS and TURBERFIELD is

$$(19) \quad \mu' = (2.792730 \pm 0.000040) \text{ (14 ppm) (inverse cyclotron; with stable orbit)}$$

which is in good agreement with the omegatron measurement.

More recently still K. R. TRIGGER [36] has shown that theoretical calculations of the BLOCH and JEFFRIES inverse cyclotron orbits yield a set of three coupled non-linear equations which predict a frequency shift dependent upon the decelerating voltage. After these corrections TRIGGER finds that the inverse cyclotron results of BLOCH and JEFFRIES are in good agreement with those of the omegatron or of COLLINGTON, DELLIS, SANDERS and TURBERFIELD. TRIGGER's corrected value is, in nuclear magnetons,

$$\mu' = 2.79267 \pm 0.00010.$$

7. - ΔE_D fine structure separation in deuterium in frequency units.

The energy separation, ΔE_D , of the $2^2P_{3/2}$ and $2^2P_{1/2}$ states of deuterium has been measured in frequency units (Table VIII) with the astonishing accuracy of ± 9 parts per million by E. S. DAYHOFF, S. TRIEBWASSER, and W. E. LAMB, Jr.,

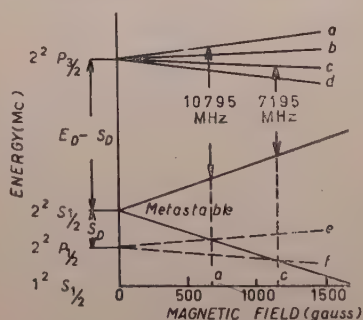
at Columbia University [37]. This marked the culmination of a remarkable series of researches on the fine structure of the hydrogen and deuterium atoms by W. LAMB, jr. with his coworkers [38-41] (*).

It was through this series of researches that the existence of the Lamb-Retherford shift, the energy difference between the $2^2S_{\frac{1}{2}}$ and $2^2P_{\frac{1}{2}}$ states, was established and its value accurately measured.

From the point of view of fundamental physics the importance of the Lamb-Retherford shift greatly overshadows the precision measurements of the fine structure separation in deuterium. This latter is, however, of prime importance as a contribution to our knowledge of the atomic constants because of its relation to the Sommerfeld fine structure constant, α , and it is therefore the only result by these workers which we shall discuss here.

LAMB and his co-workers actually obtained the separation, $2^2P_{\frac{3}{2}} - 2^2P_{\frac{1}{2}}$, in deuterium by combining the results of two independent measurements. These were (i) the $2^2P_{\frac{3}{2}} - 2^2S_{\frac{1}{2}}$ and (ii) the separation $S_D = 2^2S_{\frac{1}{2}} - 2^2P_{\frac{1}{2}}$, the famous Lamb shift. Here we shall describe only the $2^2P_{\frac{3}{2}} - 2^2S_{\frac{1}{2}}$ measurement since the Lamb shift was accomplished by similar methods. It is important to note that the $2^2S_{\frac{1}{2}}$ state is metastable with a lifetime of order 13 or 14 μ s.

TABLE VIII. - *Fine structure separation in deuterium.*



Important because of relationship to Sommerfeld fine structure constant, α .

$$\Delta E_D = \frac{1}{16} \alpha^2 R_{\infty} c \left[1 + \frac{5}{8} \alpha^2 + \frac{\alpha}{\pi} \left(1 - 5.946 \frac{\alpha}{\pi} \right) \right] \\ \cdot M_{\text{d/D}} = (10971.59 \pm 0.10) \text{ MHz (S.D.)}.$$

ΔE_D , in frequency units, is the energy separation between the $2^2P_{\frac{3}{2}}$ and $2^2P_{\frac{1}{2}}$ states in deuterium.

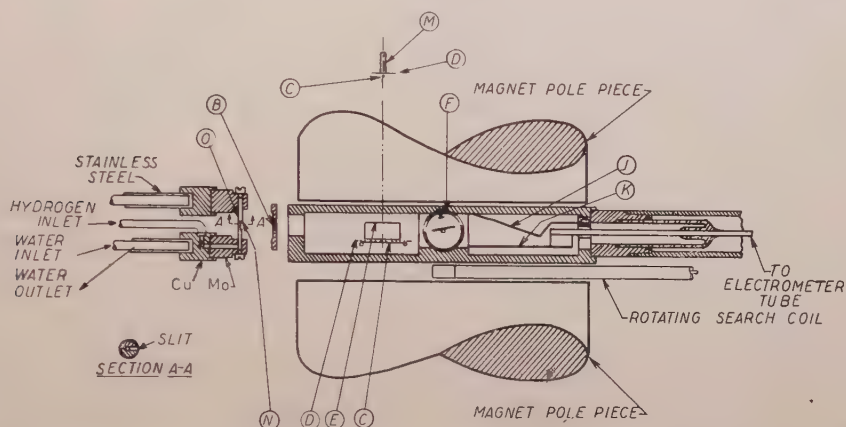
Obtained by combining the measured Lamb-Retherford shift, S_D , corresponding to $2^2S_{\frac{1}{2}} - 2^2P_{\frac{1}{2}}$ with the separation $\Delta E_D - S_D$ corresponding to $2^2P_{\frac{3}{2}} - 2^2S_{\frac{1}{2}}$. The $2^2S_{\frac{1}{2}}$ state is metastable, 30 μ s half life. $2P_{\frac{1}{2}}$ and $2P_{\frac{3}{2}}$ states are much shorter.

Table IX shows the apparatus used by LAMB and his associates. The deuterium molecules pass through a tungsten tube, *O*, heated to about 2500 °K by electrical conduction and are dissociated into monatomic deuterium. After passing through a slit, *B*, they enter a box in an accurately

(*) Parts I and II of this series by Lamb and co-workers [38, 39] should be consulted for a basic description of the apparatus.

controlled and measured magnetic field whose intensity may be varied from nearly zero to 4000 gauss. The monatomic beam is bombarded with electrons of energy 10.8 V so that excitation of the deuterium to its metastable $2^2S_{1/2}$ state occurs (*). Their lifetime is sufficient to permit a beam of deuterium atoms to persist in this excited state over a distance of

TABLE IX. — *Apparatus of W. E. Lamb Jr. and his associates.*



The dissociated deuterium atoms issue from the opening, *N*, in the electrically heated tungsten dissociator, *O*, and, after passing through slit, *B*, into the box between the magnet pole pieces, they are bombarded with 10.8 volt electrons in the U-shaped enclosure, *E*, shown also in section at *M*. The bombarding electrons for this purpose are emitted by filament, *C*, and accelerated into *E* through the grid, *D*. This bombardment excites the beam of deuterium atoms to their metastable $2^2S_{1/2}$ state. When the metastable atoms strike target, *J*, their energy of excitation ejects electrons from *J* which are collected by *K* and the resulting current is measured with an electrometer tube. In the space inside the cylindrical coaxial wave guide, *F*, however, the beam of metastable atoms is subjected to a radiofrequency electric field which if the frequency has the right critical value causes the metastable atoms to undergo transitions to the non-metastable excited states, $2^2P_{1/2}$ and $2^2P_{3/2}$; from which they decay to the ground state so rapidly that they are not detected when they reach *J*.

7 or 8 cm or more. When the metastable atoms strike a metal target, *J*, their energy of excitation is expended to eject electrons from it and these electrons

(*) Even at this low bombarding energy the transverse recoil of the atoms is sufficient to introduce an angular spread in the beam of the order of three degrees. LAMB has therefore questioned the propriety of describing it as a «beam» in comparison with the beams of the better known technique developed by RABI, MILLMAN, KUSCH and ZACHARIAS.

are collected and measured with an electrometer tube (D.C. amplifier) as a means of detecting the metastable beam. Between the exciting bombarder and the detector, however, the beam of atoms is subjected to a radiofrequency electric field and, if this frequency is exactly right, the metastable atoms undergo transitions to the non-metastable excited states $2^2P_{\frac{1}{2}}$ and $2^2P_{\frac{3}{2}}$ from which they decay with great rapidity (*) to the ground state. In this state, no excitation energy being available, they are not detected. A decrease in the response at the detector is therefore the index of a resonance between the applied RF field and an atomic transition.

The purpose of the magnetic field, as originally planned, was to split the $2^2S_{\frac{1}{2}}$ and $2^2P_{\frac{1}{2}}$ states by the Zeeman effect in order to insure longer life to the $2^2S_{\frac{1}{2}}$ state. This was before the existence of the natural (Lamb-Retherford) splitting had been established or realized. The magnetic field was also deemed useful to keep charged particles away from the detector. The third, and actually most important function of the magnetic field, however, turned out to be that of tuning the critical frequencies of the metastable atoms (through Zeeman effect) to the applied radiofrequency field, thus permitting the use of a rigorously constant, rather than a variable, applied radiofrequency which, for technical reasons, is preferable in a high precision measurement of this sort.

The measurements of DAYHOFF, TRIEBWASSER and LAMB yielded the value

$$(20) \quad \Delta E_D = (10\,971.59 \pm 0.10) \text{ MHz},$$

for the fine structure separation in frequency units between the $2^2P_{\frac{3}{2}}$ and $2^2P_{\frac{1}{2}}$ states of deuterium. This however cannot be directly equated to the familiar expression, $(\alpha^2/16)R_{\infty}c$, for the fine structure splitting because this expression is not sufficiently accurate. Three corrections are required. In the first place R_{∞} , the Rydberg constant for an infinitely heavy nucleus, must be replaced by the Rydberg constant for deuterium. This introduces the factor, M_d/D , the ratio of the mass of the deuteron to the mass of the neutral deuterium atom. Secondly, higher order terms in the Dirac expression for the fine structure splitting must be included; this adds a correction term of relative amount $(5/8)\alpha^2$. These two corrections are both implicit in the Dirac theory and their inclusion here is required by the increased accuracy of experimental techniques. The third correction represents a modification of the Dirac theory and is the result of the anomalous magnetic moment of the electron [42, 43]. It is properly identified with the Lamb-Retherford shifts in the energy of the $2^2P_{\frac{3}{2}}$ and $2^2P_{\frac{1}{2}}$ levels [44, 45]. The correct theoretical expression for the energy difference has been given by LAMB, accurate to terms of order $\alpha^6 mc^2$. This

(*) The atoms are estimated to move only a few microns in this decay time.

expression is

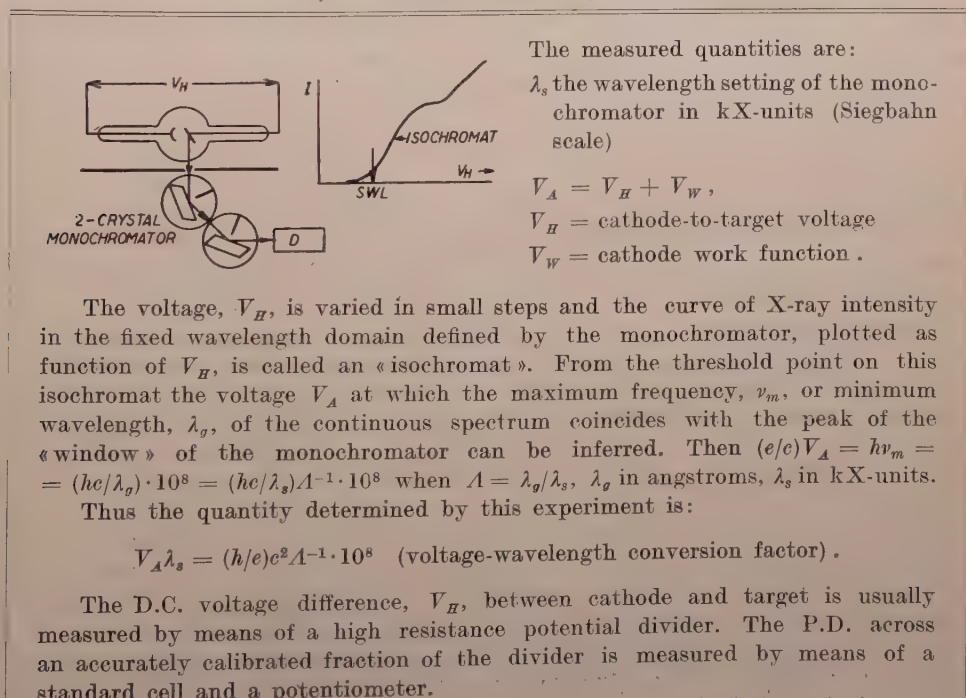
$$(21) \quad \Delta E_{\text{D}} = \left(\frac{1}{16}\right) \alpha^2 R_{\infty} c \left[1 + \left(\frac{5}{8}\right) \alpha^2 + \frac{\alpha}{\pi} \left(1 - 5.946 \frac{\alpha}{\pi} \right) \right] M_{\text{d}}/D.$$

8. - The voltage-wavelength conversion factor, $(h/e)c^2\lambda^{-1}$: short wavelength limit (SWL) of the continuous X-ray spectrum.

X-ray SWL determinations consist in exciting an X-ray tube with an extremely stable and very accurately measured D.C. voltage, V_H , and simultaneously determining with a spectrometer of highest possible resolution the minimum wavelength, λ_m , of the continuous X-ray spectrum emitted by the tube (Table X).

It has been shown [46-49] both by theoretical considerations and by internal experimental evidence that the quantum energy, $h\nu_m = hc/\lambda_m$, of the radiation at this limiting point corresponds ideally to the energy acquired by the thermally emitted cathode electrons falling through a potential difference, $V_A = V_H + V_W$, which is the sum of V_H , the measured voltage difference between cathode and target, and V_W , the work function of the thermally emitting cathode.

TABLE X. - Voltage-wavelength conversion factor by means of the short wavelength limit of the continuous X-ray spectrum.



The voltage, V_H , is varied in small steps and the curve of X-ray intensity in the fixed wavelength domain defined by the monochromator, and plotted as a function of V_H , is called an « isochromat ». From the threshold point on this isochromat one ascertains the voltage, V_A , at which the minimum wavelength component of the continuous spectrum coincides with the peak of the band-pass or « window » curve of the monochromator. For this point, conservation of energy requires the relation

$$(22) \quad (e/c)V_A = h\nu_m = (hc/\lambda_g) \cdot 10^8 = (hc/\lambda_g)A^{-1} \cdot 10^8; \quad \lambda_g \text{ in angstroms} \\ \lambda_g \text{ in kX-units.}$$

Thus the quantity determined by this experiment is:

$$(23) \quad V_A \lambda_g = (h/e)c^2 A^{-1} \cdot 10^8 \\ \text{(voltage-wavelength conversion factor in kV X-units).}$$

The D.C. voltage V_H applied to the X-ray tube terminals is usually measured by means of a high resistance potential divider, a precisely calibrated fraction of the P.D. being measured with a potentiometer and standard cell.

This experiment has always tended to yield values of h/e which were *lower* than the value required for consistency with the bulk of the data on the constants, i.e., in a direction implying *more* radiant quantum energy, $h\nu$, than the electron energy, eV_A , which produced it. Older, more obvious sources of such error have gradually been eliminated. Unfortunately the results of all of even the most recent and carefully performed experiments of this type are still somewhat incompatible (and in the same direction) with the remaining data

Table XI. — X-ray quantum limit determinations.

Experi- menters	Nominal voltage	a (volt)	hc^2/eA kV X-units	Discrepancy (ppm)	Discrepancy (volt)	Remarks
BJW ^(a)	6 112	0.27	12 370.8	— 116	-0.7 ± 0.4	W target
BS ^(b)	8 050	0.37	12 371.9	— 28	-0.2 ± 0.5	Cu target
BS ^(b)	8 050	0.37	12 371.0	— 101	-0.8 ± 0.5	{ 3 observations Mo, Ta, Au targets
BS ^(b)	8 050	0.37	12 370.1	— 174	-1.4 ± 0.5	
BS ^(b)	9 860	0.47	12 370.1	— 174	-1.7 ± 0.5	{ 2 observations Cu, Ni targets
BJW ^(a)	10 168	0.48	12 371.2	— 80	-0.8 ± 0.6	
BS ^(b)	19 600	0.96	12 371.9	— 28	-0.6 ± 1.1	W target; W fil.
BS ^(b)	19 600	0.96	12 370.1	— 174	-3.4 ± 1.1	W target; ox. cath.
FHD ^(c)	24 500	6.0	12 370.0	— 177	-4.3 ± 1.3	W target; W fil.

^(a) J. A. BEARDEN, F. T. JOHNSON, and H. M. WATTS: *Phys. Rev.*, **81**, 70 (1951).

^(b) J. A. BEARDEN, and G. SCHWARZ: *Phys. Rev.*, **79** 674 (1950).

^(c) G. F. FELT, J. N. HARRIS, and J. W. M. DUMOND: *Phys. Rev.*, **92**, 1160 (1953).

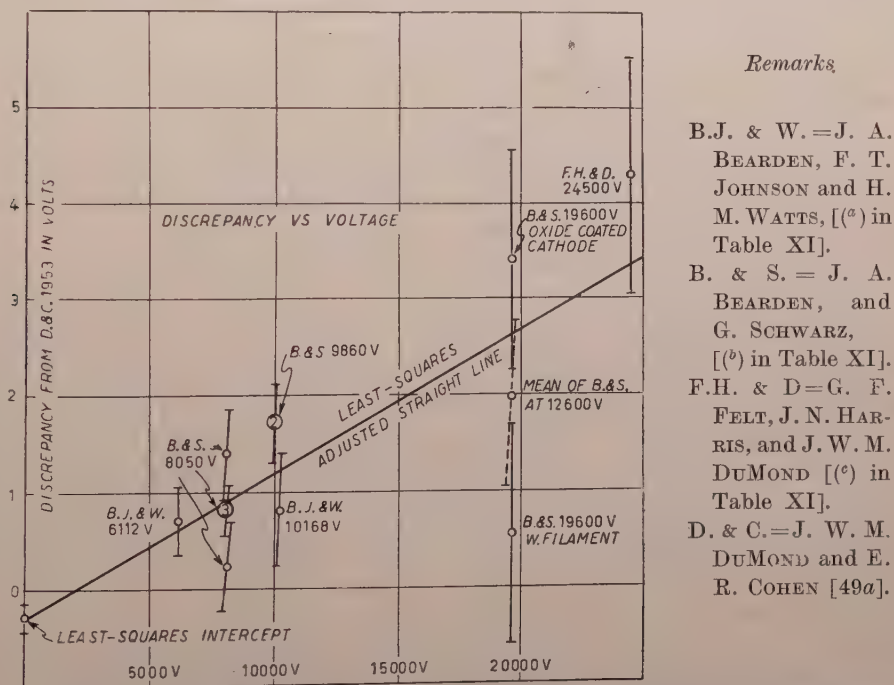
of our otherwise quite consistent least squares adjustments. The discrepancy is now roughly of the order of a part in ten thousand.

Table XI shows the results of nine determinations of the voltage-wavelength conversion factor measured at six different voltages ranging from 6112 V to 24500 V. A trend, which we believe is indicative of a systematic error more or less common to all the experiments listed, is perceptible if we plot the discrepancy in volts between the observed and computed threshold values as a function of the different experimental voltages at which they were determined. In this comparison we have based the computed values on our 1953 least squares adjusted value of the voltage-wavelength conversion factor, namely

$$hc^2/eA = 12372.2 \text{ kV X-units.}$$

The ordinates in Fig. of Table XII show the aforementioned discrepancies in volts plotted as a function of the voltage of each experiment. Where several values fall at the same point the number of these is indicated.

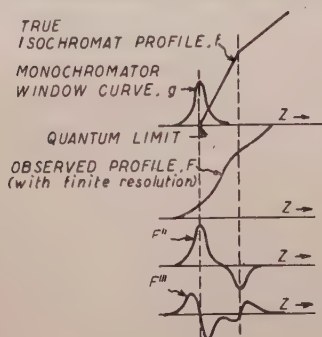
TABLE XII.



A plot of the discrepancies in volts between the observed and computed threshold voltage values for X-ray SWL isochromats taken at six different voltages and wavelengths by three different experimenters. The computed values are based on the 1953 least squares adjusted value of the voltage-wavelength conversion factor. The point marked «least squares intercept» is not one of the experimental observations.

There is a reasonably well defined trend, the discrepancy in volts tending to diminish roughly linearly with voltage, although the precision is insufficient guarantee a firm conclusion as to this linearity.

TABLE XIII. *The criterion of maximum bending to locate the quantum limit*



Basic Assumption:

— The true continuous spectrum profile for a thick target has a second order discontinuity at the quantum limit.

— The observed isochromat is the *fold* of the true isochromat into the « window curve », g , of the spectrometer.

$$F(z) = \int_{-\infty}^{z} g(x)f(z-x) dx.$$

Assume the true isochromat consists of a broken line consisting of straight segments with slopes:

$$f'(x) = a_i \quad \text{for} \quad x_{i-1} < x < x_i; \quad i = 1, 2, 3, \dots$$

Then

$$F'''(z) = g(z)f'(0) + \sum_{i=1}^{\infty} g(z-x_i)(a_{i+1} - a_i).$$

Thus each break in slope in the f -curve generates in the F'' curve a replica of the g -curve whose intensity and sign is proportional to the break. The third derivative F''' will clearly have a « zero » at each break in slope.

The criterion used in this experiment to locate the true threshold point on the « fillet » of the observed isochromat curve is to take it at the point of maximum « bending » (i.e. maximum second derivative) of the isochromat. This method (Table XIII), first proposed by DUMOND in 1937 and used in all the precision determinations which we are considering here, is based on the assumption that the true continuous spectrum profile for a thick target X-ray tube has a simple second order discontinuity at the quantum limit. The observed isochromat, F , is the « fold » of the true spectral profile into the monochromator « window » curve, g .

$$(24) \quad F(z) = \int_{-\infty}^{z} g(x)f(z-x) dx.$$

If we approximate the shape of the true spectral profile, f , in the neighborhood of the limit by a broken straight line with straight segments having finite slopes, a_i ,

$$(25) \quad f'(x) = a_i \quad \text{for} \quad x_{i-1} < x < x_i; \quad i = 1, 2, 3,$$

then differentiating our fold equation, (24), twice one obtains

$$(26) \quad F''(z) = g(z)f'(0) + \sum_{i=1}^{\infty} g(z - x_i)(a_{i+1} - a_i),$$

from which we see that each break in slope in the true spectrum (including the second order discontinuity at the quantum limit) generates in the F'' curve a replica of the g -(or window) curve whose intensity and sign is proportional to the magnitude of the break in slope. The third derivative, F''' , of the isochromat will clearly have a «zero» at each break in slope.

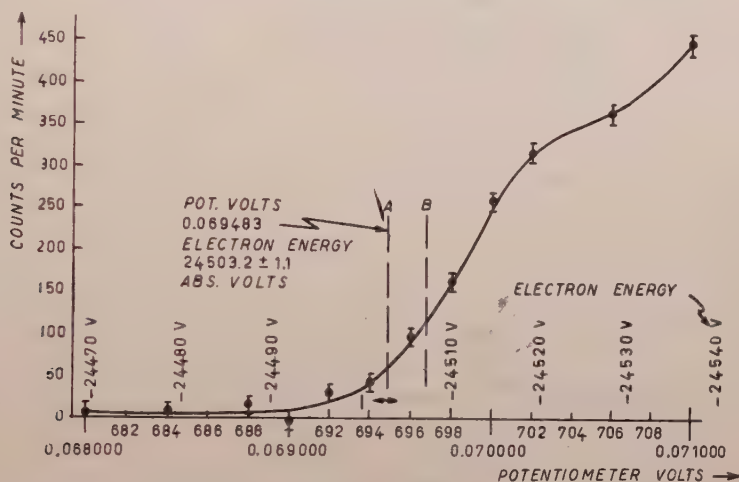


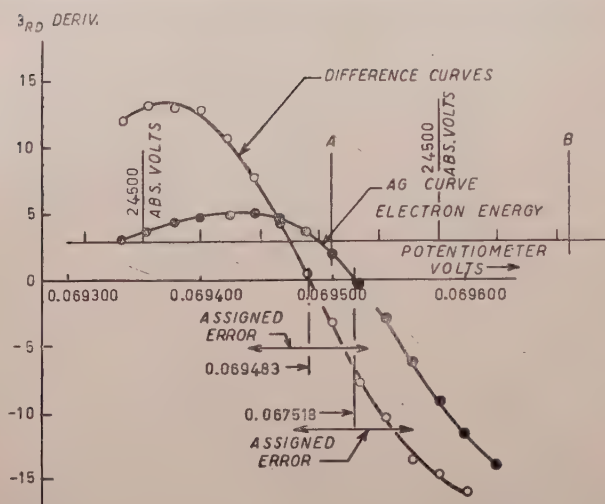
Fig. 3. — One of the isochromats obtained by FELT, HARRIS and DUMOND at 24500 volts.

Fig. 3 shows one of the isochromats obtained at the highest voltage, 24500 V, listed in the preceding tabulation. The point marked *A* is the point of maximum bending; the point *B*, however, is the required position of the quantum limit for consistency with the 1953 least squares adjustment.

The figure of Table XIV shows how the point of maximum bending (*A* in Fig. 3) was determined; by plotting the third derivative of the isochromat and locating its zero point (*). The point *B*, to the extreme right, is the required position for consistency with the 1953 adjustment.

(*) The third derivative was obtained by a numerical interpolation method using for each value of F''' an array of points at equidistant abscissa spacings on the smoothed isochromat curve. The point at which F''' was to be evaluated was always at the center of this array. The method yields the third derivative of a high order polynomial fitted to the points of the smoothed curve but is of course no more precise than the smoothing of the curve is reliable. The assigned uncertainty (indicated by the arrows in this and the previous slide) was therefore based on variations in the location of the point $F''' = 0$ when the curve was smoothed in different trials and by different people.

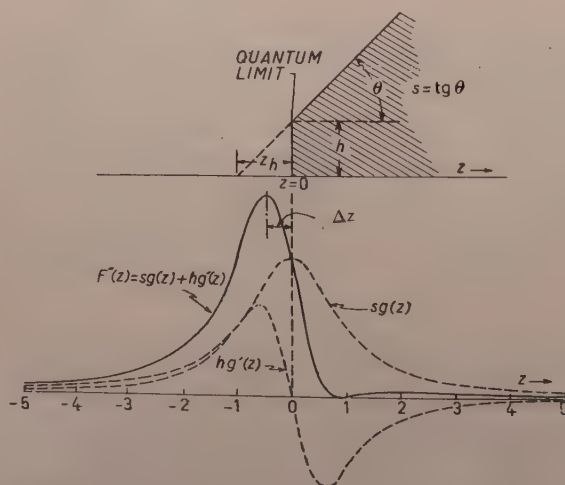
TABLE XIV.



The curved loci are the third derivatives of isochromats taken at 24500 volts. The locus marked « difference curves » resulted from isochromats whose intensities were the differences between observations with P. A. Ross balanced filters. The locus marked « AG curve » was observed through a single silver filter. The upper of the two abscissa scales shows the absolute voltage, each division being one volt.

The systematic trend indicated in the preceding tables and figures strongly suggesting a systematic error might be explicable if we postulate that the ideal structure of the quantum limit consists of a superposition of a first and a second order discontinuity as shown in the diagram of the figure of Table XV.

TABLE XV.



The diagram shows the postulated precipice at the quantum limit of the continuous X-ray spectrum. If this postulate is correct, the quantum limit consists of a superposition of a first and a second order discontinuity. The lower curves show the two resulting components in the second derivative of the isochromat which will be generated, $hg'(z)$ by the first order discontinuity, $sg(z)$ by the second order discontinuity together with their sum, $F''(z)$, whose peak will be shifted by an amount, Δz , from the true quantum limit position.

Referring to the lower part of that figure, if h is the height of the precipice, if $s = \operatorname{tg} \theta$ is the slope above it and if $z_h = h/s$ is what we have called the « overshoot », it is easy to show that

$$(27) \quad F''(z) = sg(z) + hg'(z) = s[g(z) + z_h g'(z)].$$

Clearly, whereas the second order discontinuity generates a g -curve, the first order discontinuity generates a curve which is the first derivative of the g -curve. (This follows because the first order discontinuity or step function, considered by itself, is the limiting case of two equal breaks in slope of opposite sign which have approached indefinitely close to each other and have become indefinitely large.) The superposition of these two curves, the primitive g -curve and its first derivative, may indeed result in a peak in the $F''(z)$ which is considerably shifted from the true quantum limit in just the direction which the observations show. Such a superposition resulting in the shift, Δz , is illustrated in the lower curves of the figure of Table XV. It turns out that if we assume the postulated overshoot, z_h , expressed in volts to be independent of the voltage at which the experiment is performed, then to explain the large shift (of order 4 or 5 V) observed at 24500 V we must assume z_h so large that a vestige of the precipice would almost certainly start to manifest itself in the isochromats taken at the lowest voltages. At these lowest voltages the monochromator pass band widths (in volts) are narrow enough so that one should see a rounded hump (convex upward) on the isochromat corresponding to the brink of the precipice in the true spectrum. Nothing like this, however, has been reported.

If then we are to explain the observed systematic trend of the results by the postulated precipice, it is necessary to assume that the overshoot, z_h , expressed in volts *decreases with decreasing voltage*. This is however not at all implausible since another feature, the position of the Ohlin irregularities, is known to be voltage dependent; its distance expressed in volts from the quantum limit decreases with decreasing voltage. The available data are insufficiently precise to yield information on the overshoot, Δz , as a function of voltage, which can be safely used to correct the experimental data. A more complete analysis of the theory of the continuous X-ray spectrum from thick targets is much needed.

Unfortunately there is little hope of improving the spectral resolving power in this experiment greatly beyond what has been already attained since the present results are already close to the theoretically attainable limit with perfect crystals according to the « dynamical theory » of selective X-ray reflection.

The conclusions to be drawn seem to be:

1) The most important residual source of systematic error in the short wavelength limit experiment comes from uncertainties, because of limited re-

solving power, as to how the true limit position should be estimated from the isochromat profile.

2) The X-ray isochromats obtained at the lowest voltages seem more likely to yield the most reliable results.

The nine determinations which were made at the lowest voltages (between 6000 V and 11000 V) form a cluster which is rather widely separated from the results obtained at the two higher voltages. In view of our ignorance of how best to correct for the above described systematic trend we shall adopt the weighted mean of this group of nine results made at the lowest voltages.

TABLE XVI. - *Selection of data on voltage-wavelength conversion factor.*

The determinations made at the <i>lowest voltages</i> seem less likely to be in error from the systematic shift which we have ascribed to the postulated precipice at the quantum limit. The nine lowest voltage precision determinations are given below					
Experimenter		Nominal voltage	$hc^2/e\lambda$ (kV X-units)	Number of observations	Weight
(a), (b) see Table XI.	BJW ^(a)	6112	12370.8	1	1
	BS ^(b)	8050	12371.9	1	1
	BS ^(b)	8050	12371.0	3	3
	BS ^(b)	8050	12370.1	1	1
	BS ^(b)	9860	12370.1	2	2
	BJW ^(a)	10186	12371.2	1	1
Weighted mean value:			(12370.8 \pm 0.2) kV X-units (S.D. by external consistency)		
DUMOND and COHEN					
1953 [49a] adjusted value:			(12372.2 \pm 0.4) ♪		

Table XVI presents these data which result in a weighted mean value of the voltage-wavelength conversion factor

(28) (12370.8 ± 0.2) kV X-units (S. D. by external consistency) .

This still differs from the least squares adjusted value of 1953

(29) (12372.2 ± 0.4) kV X-units

by an uncomfortably large amount. These two numerical values are not statistically independent so that care must be exercised in interpreting the significance of their disagreement. In Dr. COHEN's paper the correct method of assessing the seriousness of such a discrepancy between an input quantity and its adjusted output value in a least squares adjustment will be discussed.

PART II

INPUT DATA TREATED AS EXACT

9. — M_a , atomic weights by method of nuclear reaction energies.

In a nuclear reaction between a bombarding particle, x , and a target nucleus, X :



a final particle, y , with kinetic energy, T_y , and a final nucleus, Y , with kinetic energy, T_Y , are produced. Conservation of energy requires that the total of the kinetic and rest-mass energies before and after the reaction shall be equal.

$$(31) \quad (T_x + m_x c^2) + (M_X c^2) = (T_Y + M_Y c^2) + (T_y + m_y c^2),$$

The net gain in kinetic energy of the product particles above that of the input reactant particles, called the « Q » of the reaction, is measured.

$$(32) \quad Q = T_Y + T_y - T_x = (M_X + m_x - M_Y - m_y) c^2.$$

More than one nuclear reaction is needed to yield enough simultaneous equations such as this one, (32), to obtain the mass difference between a pair of particles, as for example, the neutron and the proton. However a great number of nuclear reactions in the light elements has been precisely measured; so many in fact that the available information on nuclear Q -values affords a high degree of overdetermination for establishing mass differences of all the isotopes of all the light elements from the neutron through sulphur ($Z = 16$). Since this includes ^{16}O , the isotope which *by definition* has atomic mass exactly 16 on the physical scale, the method affords an extremely precise set of atomic mass values good to a few parts in a million for all these light nuclei. This corresponds to determining the Q -values of the reactions with an accuracy of the order of 1 kV. LI, WHALING, FOWLER, and LAURITSEN [50] in an important study in 1951 used the Q -value of 57 different nuclear reactions to establish a table of masses of 31 isotopes between $Z = 0$ (the neutron) and $Z = 9$ (fluorine). VAN PATTTER and WHALING [51] in 1954 list separately all the Q -value determinations that have been made on no less than 474 nuclear reactions. About 600 independent Q determinations are tabulated by the.m

To the date of this writing no evidence has appeared significantly discordant with the mass values and their error measures as given by LI, WHALING, FOWLER and LAURITSEN though some work claiming slightly smaller error measures has recently been published by WAPSTRA [52]. The precision of the mass values given by LI, WHALING, FOWLER and LAURITSEN is amply sufficient for the purpose we shall make of them in determining the general constants of physics. We therefore adopt the values given in the Table XVII.

TABLE XVII. - *Atomic masses by measurement of nuclear reaction energies.*

See [50], [51], [52], [52a].

$$H = 1.008142 \pm 0.000003 \text{ (3 ppm) (physical scale)}$$

$$H/M_p = 1.00054461$$

$$D = 2.014735 \pm 0.000006 \text{ (3 ppm) (physical scale)}$$

$$D/M_d = 1.00027244$$

H/M_p and D/M_d computed using atomic weight of electron $Nm = 5.4875 \cdot 10^{-4}$.

Nm may be obtained from the isotopic shift in the spectra of H and D, the effect called by Sommerfeld the « Mitbewegung des Kerns ». It can also be determined by comparison of the cyclotron frequencies of electron and proton.

These value are based on the work of these authors combined with Nm , the atomic mass of the electron, which is required in order to compute M_p and M_d , the atomic masses of the proton and the deuteron.

(33) Atomic mass of electron, $Nm = 0.000549$ (physical scale).

Information on the atomic mass of the electron is available from two independent sources [53-56], (i) the isotopic shift in the spectrum of hydrogen and deuterium caused by the effect known in German as the « Mitbewegung des Kerns » and (ii) the comparison of the cyclotron frequency of the electron with the cyclotron frequency of the proton.

10. - R_∞ , Rydberg constant for infinite mass (taking account of Lamb shift).

E. R. COHEN [53] has reanalyzed the spectroscopic data of W. V. HOUTON [57], of DRINKWATER, RICHARDSON and WILLIAMS [58], and of D. Y. CHU [59] in the light of our present knowledge of the Lamb shift and has obtained

$$(34) \quad R_\infty = (109737.309 \pm 0.012) \text{ cm}^{-1} \text{ } (\pm 0.11 \text{ ppm}).$$

The Rydberg is an auxiliary constant which plays a role of great importance since it determines with great accuracy an important function of two of our unknowns, α and e .

$$R_{\infty} = 2\pi^2 m e^4 / h^3 c = m c^2 \alpha^3 / 4\pi e^2 .$$

Once the adjusted values of α and e have been determined, the value of these and R_{∞} can be used to compute Planck's constant, h , and the electron mass, m , from

$$h = 2\pi e^2 / \alpha c ,$$

$$m = 4\pi e^2 R_{\infty} / \alpha^3 c^2 .$$

11. - μ_e/μ'_p , ratio of electron magnetic moment to proton magnetic moment.

11'1. *Method of Gardner and Purcell* [54, 55] (Table XVIII). - I have described the measurement of the proton magnetic moment in terms of the nuclear magneton by comparison of the *proton cyclotron frequency* with the proton magnetic resonance frequency in the same magnetic field. At Harvard University a similar experiment has been performed on the *cyclotron frequency of the electron* compared with the proton magnetic resonance frequency. This yields the proton magnetic moment in terms of the Bohr magneton.

The cyclotron frequency, ω_e , of a free electron in a magnetic field, B , is given by

$$(35) \quad \omega_e = eB/mc \quad (e \text{ expressed in esu}).$$

The proton precession frequency, ω_p , is given by

$$(36) \quad \omega_p = \gamma'_p B = 2\mu'_p B/\hbar ,$$

where γ'_p is the gyromagnetic ratio of the proton (uncorrected for diamagnetism) and μ'_p is the proton magnetic moment (similarly uncorrected.) The ratio ω_p/ω_e is therefore

$$(37) \quad \omega_p/\omega_e = 2\mu'_p mc / e\hbar = \mu_p/\mu_0 ; \quad \mu_0 = \text{Bohr magneton} \\ = e\hbar/(2mc) .$$

This ratio is seen to be μ'_p , the magnetic moment of the proton, expressed in Bohr magnetons, $\mu_0 = e\hbar/2mc$, a fundamental constant. To obtain μ'_p/μ_e from these results we must know μ_e/μ_0 the (« anomalous ») ratio of the electron magnetic moment to the Bohr magneton which modern quantum-electro-

dynamical theory has shown to differ slightly from unity. Theory gives for this

$$(38) \quad \mu_e/\mu_0 = (1 + \alpha/2\pi - 2.973\alpha^2/\pi^2) = 1.00114536 \quad (\text{if } \alpha^{-1} = 137.037 \text{ (*)}).$$

If we combine the results of this experiment on ω_p/ω_e with a knowledge of γ'_p , from the aforementioned work of THOMAS, DRISCOLL, and HIPPLE, our first two equations, Eqs. (35) and (36), show that we can calculate e/mc the charge-to-mass ratio of the electron (expressed in emu) from the relation

$$(39) \quad \omega_p/\omega_e \gamma'_p = e/mc.$$

Furthermore if we combine ω_p/ω_e from the results of this experiment with ω_e/ω_p from the results of the SOMMER, THOMAS, and HIPPLE experiment described above we can obtain ω_e/ω_c , the ratio of the respective cyclotron frequencies of electron and proton and this gives directly m_p/m , the ratio of the mass of the proton to the mass of the electron

$$(40) \quad \omega_e/\omega_c = (\omega_e/\omega_p)/(\omega_c/\omega_p) = m_p/m.$$

TABLE XVIII. — Ratio proton resonance frequency to electron cyclotron frequency, ω_p/ω_e .

See [54], [55].

The electrons drift in helical paths in microwave field in wave guide executing turns at the cyclotron frequency,

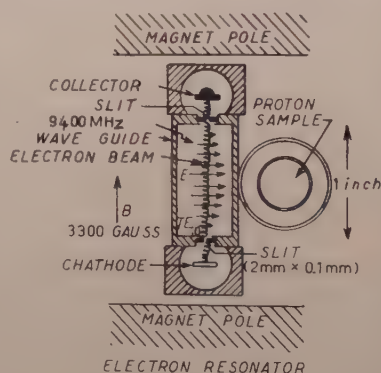
$$\omega_e = eB/mc.$$

If ω_e matches exactly the microwave input frequency the electrons gain energy and miss the second slit and a dip in current would indicate resonance. For very low cathode voltage, $\simeq V_a$, however, space-charge effects produced a current *peak* at resonance.

Results:

$$\omega_e/\omega_p = \mu_0/\mu'_p = 657.475 \pm 0.008 \quad (\text{without diamagnetic correction})$$

$$\omega_e/\omega_c = m_p/m = 1836.12 \pm 0.03$$



The cyclotron frequency of the electron was measured by providing slits, 2 mm \times 0.1 mm, on opposite sides of a rectangular shorted wave guide of 1 \times 0.5 inch internal cross-section and supplied with microwaves of frequency

(*) This value of α is practically beyond question. Our least squares analysis yields $\alpha^{-1} = 127.0373 \pm 0.0006$. A change of 0.01 in α^{-1} produces a change of less than 10^{-7} in μ_e/μ_0 .

9400 MHz in the TE_{10} mode so that a ribbon shaped beam of slow electrons drifting across the 1 inch dimension of the guide from one slit to the other crossed in a region of voltage maximum of the microwaves. The electrons were supplied by an oxide coated cathode in a copper cavity behind one of the slits and were collected by an electrode in a second copper cavity behind the other slit. This equipment was placed in a magnetic field of 3300 gauss, between the poles of an electro-magnet with the direction of the field parallel to the general direction of motion of the electron from slit to slit across the wave guide. Closely adjacent to the wave guide between the magnet poles was placed the proton resonance head. This operated on a frequency of 14.24 MHz. This frequency was multiplied 657 times for comparison with the electron cyclotron frequency in the wave guide. The positions of proton resonance head and wave guide between the magnet poles could be interchanged so that by averaging the results before and after such interchange the effect of any slight difference in magnetic field intensity at these two elements could be compensated.

The electrons drift in helical paths from one slit to the other across the wave guide executing the turns of their helices at the cyclotron frequency, $\omega_e = eB/mc$. If this frequency matches exactly the microwave frequency of the electric vector in the wave guide the electrons gain energy at each turn and their helical trajectories will expand so that many of them will fail to pass through the second slit. It was thus anticipated that resonance would be recognized by a decrease in current to the collector. For very weak electron accelerating voltage, $-V_a$, at the cathode however, space charge effects produced a current *peak* at resonance (*).

The final value assigned by GARDNER [55] was

$$(41) \quad \mu_0/\mu'_p = \omega_e/\omega_p = 657.475 \pm 0.008,$$

(*) To make the resonance as sharply defined as possible it is desirable to have very slow electrons so that a maximum number of cyclotron cycles will be executed during the transit time from slit to slit in the region of the rf. field.

The cathode was held more negative than the wave guide by a voltage, V_a , adjustable from 0 to 5 V, and the collector was maintained approximately 20 V positive relative to the guide so as to collect all the electrons passing through the second slit. When V_a was approximately 5 V the expected dip in anode current (from approximately 0.4 μA to 0.3 μA) was observed at resonance. However it was found that peaks instead of dips occurred at resonance, if V_a was less than about 3 V. The peaks were considerably sharper than the dips, having a width of order 0.5 G contrasted with 5 G for the dips. The anode current under these circumstances was less than 0.0005 μA when away from resonance. This unexpected behavior was attributed to space charge limitation of the electron current through the guide save at resonance. The electrons having the slowest transverse velocity across the guide would be the ones most responsible for this space charge limitation and these are also the ones which at resonance are acted upon for the longest time by the microwaves. The resulting

without the diamagnetic correction to the field of the proton for the electrons in the hydrogen molecule. If we calculate ω_e/ω_c by equation (40) using ω_e/ω_d (Eq. (41)) and the results of SOMMER, THOMAS and HIPPLE for ω_c/ω_p , one obtains for the ratio of the rest masses of proton and electron

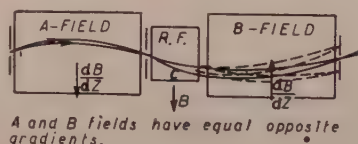
$$(42) \quad \omega_e/\omega_c = m_p/m = 1836.12 \pm 0.03.$$

11'2. *Method of Koenig, Prodel and Kusch.* - A quantity which is closely related to the one measured by GARDNER and PURCELL is the ratio, μ_e/μ'_p , of the electron magnetic moment to the proton magnetic moment (recall that we are using μ'_p for the apparent moment before correction for the diamagnetic effect; μ_p is the corrected moment). This ratio was measured by KOENIG, PRODELL and KUSCH [60] (Table XIX) at Columbia University with such high accuracy (an error of ± 0.6 ppm) that it can be very safely treated as a fixed auxiliary constant among the input data of our present least squares analysis. The well known molecular beam method [61] for measuring nuclear magnetic moments was used in this measurement.

TABLE XIX. - Ratio electron magnetic moment to proton magnetic moment, μ_e/μ'_p .

S. H. KOENIG, A. G. PRODELL and P. KUSCH [60] used the well-known method of RABl, MILLMAN, KUSCH and ZACHARIAS [61].

A beam of H-atoms is deflected downward in the A-field and upward in the B-field by an equal amount unless the magnetic moment of the atoms is changed by the R.F. present in the C-field, in which case the atoms miss the final slit.



3655 MHz R.F. used to induce hyperfine structure transitions. From the transition frequency of the line $(1, 0 \longleftrightarrow 1, -1)$ in the field B together with the proton nuclear magnetic resonance frequency for the same field B, the ratio, g_p/g_j , of the proton g -value to the g -value for the hydrogen atom in the $^2S_{1/2}$ state, the latter closely related to the electron spin g -value, g_s , was measured with the result:

$$g_s/g_p = M_p/(Nm\mu')(1 + \alpha/2\pi - 2.973\alpha^2/\pi^2) = 658.2288 \pm 0.0004.$$

Here M_p = atomic weight of proton, Nm = atomic weight of electron, μ' = magnetic moment of proton (uncorrected for diamagnetism) expressed in nuclear magnetons and the trinomial is μ_e/μ_0 , the electron magnetic anomaly ratio, 1.00114536.

From this $\mu_0/\mu'_p = M_p/(Nm\mu') = 657.4758 \pm 0.0004.$

expansion of their orbits when resonance obtains would reduce the space charge density and thus permit an increase in current across the guide on the part of other electrons (presumably those directed most nearly parallel to the magnetic field). Because of its superior sharpness, the peak attributed to the suppression of space-charge limitation was the one exclusively used for the measurements.

An atomic beam passes successively through three magnetic fields; the first and last, (the A and B fields), are inhomogeneous with gradients in opposite directions, while the intermediate field is uniform. Because of the interaction of the atomic dipole moment and the inhomogeneous magnetic field, an atom will suffer a deflection in passing through the A field. The B field then impresses on the atom a deflection in the opposite direction. Whatever the magnetic moment of the atom may be (as long as it is the same in both fields), the two deflections will compensate each other and the atom will return to the instrument's axis after passing through the two fields. If, however, during the time of transit through the intermediate C field, a transition is induced in the atom so that its magnetic dipole moment is altered, such atoms will not receive the correct compensating deflection in the B field and will fail to pass through the exit slit of the instrument. A magnetic field of frequency 3655 MHz perpendicular to the direction of the static field was used to induce the transition between hyperfine structure levels in hydrogen in $^2S_{\frac{1}{2}}$ state. The transition frequency of the line $(1, 0 \leftarrow \rightarrow 1, -1)$ was measured and from this, and measurements of the proton nuclear magnetic resonance frequency in the same magnetic field (THOMAS, DRISCOLL and HIPPLE) g_p/g_s could be calculated. g_p is the proton g -value while g_s , the g -value for the hydrogen atom in the $^2S_{\frac{1}{2}}$ state, is closely related to the electron spin g -value, g_s . The experimental result obtained by KOENIG, PRODELL and KUSCH was (before the correction for diamagnetism in the proton resonance oil sample),

$$(43) \quad g_s/g_p = [M_p/Nm\mu'](1 + \alpha/2\pi - 2.973\alpha^2/\pi^2) = 658.2288 \pm 0.0004,$$

in which M_p is the atomic weight of the proton, N is Avogadro's number, m the mass of the electron, μ' the magnetic moment of the proton (uncorrected for diamagnetism) expressed in nuclear magnetons, and the trinomial in the parenthesis is μ_e/μ_0 , the correction factor for the anomalous magnetic moment of the electron [42, 43]. This can be computed from the value $\alpha^{-1} = 137.037$, with ample accuracy (see Eq. (38) above) to place μ_e/μ_0 in the category of auxiliary fixed constants. The result is

$$(44) \quad \mu_0/\mu'_p = M_p/Nm\mu' = 657.4758 \pm 0.0004.$$

11'3. Resonant cavity method of Beringer and Heald. — BERINGER and HEALD [62] (Table XX) have measured the ratio of proton moment to electron moment using a microwave absorption technique. Since this method is basically distinct from the molecular beam method used by KOENIG, PRODELL and KUSCH, a comparison of the two results is useful. Hydrogen atoms are contained in a resonant cavity placed in a uniform magnetic field. This field produces a Zeeman splitting of the atomic energy levels and the strength of this field

is varied until the Zeeman splitting corresponds to the resonant frequency of the cavity. The absorption of energy by the atoms at this resonance reduces the energy transmitted through the cavity from a klystron oscillator to a detector. The magnetic field in the experiment is measured by a proton resonance probe. Thus the magnetic moment of the proton and the electron are directly compared. The result, uncorrected for diamagnetism in a spherical sample of mineral oil is

$$(45) \quad \mu_e/\mu'_p = 658.2298 \pm 0.0003,$$

where the quoted error is a statistical standard deviation of the mean of 34 observations after 10 discordant data were rejected. This result is 1.5 ppm larger than KOENIG, PRODELL and KUSCH's measurement (43) and is twice as large as the standard error of that difference computed from the quoted errors.

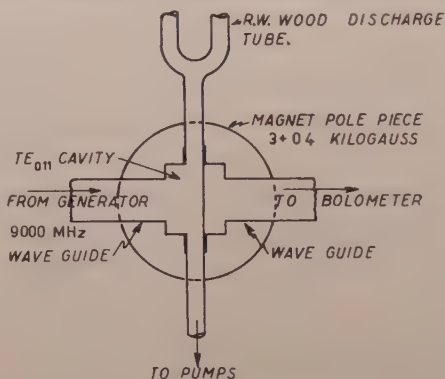
TABLE XX. - Ratio of electron magnetic moment to proton magnetic moment. μ_e/μ'_p .

Hydrogen atoms in resonant R.F. cavity are in a uniform magnetic field which produces a Zeeman splitting of the atomic energy levels. Field is varied until level splitting corresponds to a resonant frequency of the cavity. Absorption of R.F. energy at resonance reduces transmission through cavity and response of bolometer detector. Magnetic field stabilized and measured by proton resonance probes.

Result:

$$\mu_e/\mu'_p = 658.2298 \pm 0.0003 \text{ (mean of 34 observations)}$$

1.5 ppm larger than Koenig, Prodehl and Kusch value (twice S.E. of difference).



In obtaining the result of KOENIG, PRODELL and KUSCH, (Eq. (44)), to compare with the above measurement of GARDNER and PURCELL we made use of the theoretical value of the anomalous moment of the electron (Eq. (38)). We can also reverse the procedure and calculate the anomalous electron moment by combining GARDNER and PURCELL's results with the measurements of KOENIG, PRODELL and KUSCH or BERINGER and HEALD. In either case we obtain the result

$$(46) \quad \mu_e/\mu_0 = 1.001147 \pm 0.000008 \text{ (experimental value)}$$

where the error is entirely due to the GARDNER and PURCELL value and masks the difference between the two values of μ_e/μ'_p . The agreement between this value of μ_e/μ_0 and the theoretical value 1.00114536 is excellent and serves as a verification of the validity of quantum electrodynamics.

12. - Recent measurements of the velocity of light.

Table XXI shows the results of nine independent determinations of the velocity of light (or of radio waves) made since 1949. All these methods indicate quite unequivocally that the earlier weighted average value arrived at by BIRGE, based chiefly on earlier measurements by MICHELSON, PEASE and

TABLE XXI. - Recent measurements of the velocity of light.

Author	Date	Method	c in km s ⁻¹	Remarks
ASLAKSON. . . .	1949	«Shoran»	299 792 ± 3.5	FLCR = fixed length
HANSEN and BOL	1950	FLCR	299 789.3 ± 1.2	cavity resonance
ESSEN	1950	VLCR	299 792.5 ± 1.0	VLCR = variable
BERGSTRAND . .	1951	Geodimeter	299 793.1 ± 0.32	length cavity reso-
FROOME	1952	FSMWI	299 792.6 ± 0.7	nance
MACKENZIE . . .	1953	Geodimeter	299 792.4 ± 0.5	FSMWI = free space microwave interfero-
FROOME	1954	FSMWI	299 793.0 ± 0.3	
PLYLER, BLAINE and CONNOR .	1955	IRSP	299 792 ± 6	meter
FLORMAN	1955	FSMWI	299 795.1 ± 1.9	IRSP = infrared spe-
				ctrometer

C. I. ASLAKSON: *Nature*, **164**, 711 (1949); K. BOL: *Phys. Rev.*, **80**, 298 (1950); L. ESSEN: *Proc. Roy. Soc., A* **204**, 260 (1950); *Nature*, **167**, 758 (1951); E. BERGSTRAND: *Ark. f. Fys.*, **2**, 119 (1950); **3**, 479 (1951); K. D. FROOME: *Proc. Roy. Soc., A* **213**, 123 (1952); **A 223**, 195 (1954); I. C. C. MACKENZIE: *Ord. Surv. Prof. Papers* 19, H. M. Stat. Office (1954); E. K. PLYLER, L. R. BLAIN and W. S. CONNOR: *Journ. Opt. Soc. Am.*, **45**, 102 (1955); *U. S. Nat. Bur. Std. Tech. News Bull.*, **39**, 1 (1955); E. F. FLORMAN: *U. S. Nat. Bur. Std. Tech. News Bull.*, **39**, 1 (1955).

PEARSON [63] with the rotating mirror method in an evacuated tube, and by ANDERSON [64] using Kerr-cell modulation, namely 299 776 km s⁻¹, was low by about 16 or 17 km s⁻¹. The newer values (those after 1948) are not all of equal reliability or accuracy nor are they all completely in agreement, and in particular the HANSEN and BOL result [65] disagrees with the others by about 3 km s⁻¹, a disagreement which, though small judged by earlier standards, is uncomfortably large relative to the claimed probable errors. A plausible explanation for this discrepancy has been suggested by E. S. DAYHOFF (*).

(*) In this experiment the true electrical diameter of the cavity is greater than the mechanical diameter by an amount of the order of magnitude of the skin depth of the walls, a depth which depends of course on the frequency of the particular mode of oscillation which is being excited. The possible presence of a film of silver sulphides of unknown thickness with a conductivity and a dielectric constant differing from

Of the determinations listed on this slide probably the most accurate and reliable are (i) those of BERGSTRAND [66] in Norway and of MACKENZIE [67] in Scotland, each using Kerr cell modulated visible light over long light paths and employing Bergstrand's highly ingenious «Geodimeter» and (ii) those of ESSEN [68] and of FROOME [69], ESSEN (*) using microwave cavity resonance and FROOME the free space microwave interferometer. These results are all in excellent agreement.

I shall only describe one of these methods, that of K. D. FROOME at the National Physical Laboratory, England.

The four-horn Fraunhofer diffraction microwave interferometer of K. D. FROOME is shown schematically in Fig. 4. The source of microwaves is a Pound stabilized reflex Klystron oscillator with a frequency of 24005 MHe corresponding to a wavelength of about 1.25 cm. The accuracy of the frequency measurement is about one part in 10^8 . Energy from the oscillator passes to a hybrid junction (« magic T ») which serves as a beam divider, from which it passes through two long wave guide arms to the pair of transmitting horns. The matching stub and phase shifter (1) to the left of the beam divider, together with a « constant phase auxiliary interferometer » (c.p.i.) constitute a device (+) for altering the amplitude of the energy transmitted down this arm without producing a phase displacement. The phase shifter (2) to the right of the beam divider, together with the variable attenuator, is required in order to adjust and balance the position of the first interference minimum.

The movable part of the interferometer situated between the transmitting horns consists of a pair of receiving horns mounted on a carriage constructed almost entirely of silica tubes (for thermal stability) and arranged to travel

the values for bulk silver will affect the observed resonant frequency of the cavity. Correction for this should increase the Hansen and Bol value of the velocity slightly. It has been suggested in a private communication by E. S. DAYHOFF that the mechanical effect of polishing the silver-plated surface may cold-work the metal and thus greatly decrease its conductivity in an extremely shallow layer. It is unfortunate that Hansen and Bol only made measurements at just enough frequencies to determine c in the absence of such anomalous skin effects. In any precision measurement it is always a better policy to overdetermine the measurements in an effort to uncover unsuspected systematic errors.

(*) In a recent communication ESSEN informs me that the estimated standard deviation of $\pm 1 \text{ km s}^{-1}$ in his 1950 determination contained an allowance for possible systematic error and that the standard deviation computed from only the statistical variance of his data would be nearer $\pm 0.3 \text{ km s}^{-1}$.

(+) This ingenious device splits the input wave into two components of equal amplitude in two different paths. These components are subsequently recombined after a change of phase brought about by an increase in the path length for one path, and an exactly corresponding decrease in the path length for the other. The two equal vectors representing the phases of the two components are thus rotated in opposite directions through the same angle so that the direction of their resultant is unchanged while its amplitude is reduced.

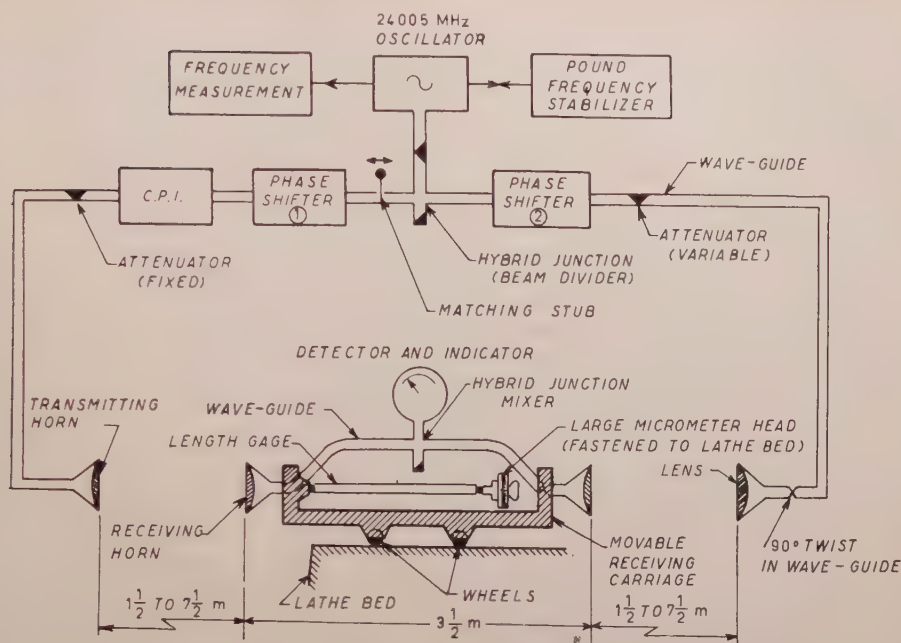


Fig. 4. — Microwave interferometer of K. D. Froome.

on ways through a path of about one meter. The two received signals are mixed to produce interference, and detected by means of a simple super-heterodyne arrangement; the output is rectified and indicated on a milliammeter. An interference minimum is then detected as minimum current through the meter and the carriage can be set on a minimum to better than one micron.

To make a wavelength measurement the exact displacement of the carriage corresponding to 81 wavelengths (162 minima) is measured to one quarter micron by means of end-contact gauges.

FROOME stated that the 24005 MHz equipment is merely a prototype for the investigation of sources of inherent error. The conditions were, therefore, deliberately chosen to cause errors; as for example the random effects arising from reflections in the rather small room. Nevertheless the apparatus was found to be capable of an accuracy of one part in 10^6 for the velocity measurements. Much better results are anticipated, therefore, with the final equipment which is to operate at 70000 MHz ($\lambda = 4$ mm) over a path difference of 1000 minima in a much larger room. Ten observations with the present prototype have been reduced to yield a preliminary value for the

free-space velocity of electromagnetic waves in vacuo of

$$(47) \quad c = (299793.0 \pm 0.3) \text{ km s}^{-1}.$$

Space limitations preclude description of many details and refinements to be found in the original papers and in particular the study of corrections for refractive index of the air and water vapor given in two papers by ESSEN and FROOME [70, 71].

REFERENCES

- [1] R. T. BIRGE: *Reports on Progress in Physics*, **8**, 90 (1941).
- [2] A. O. NIER: *Phys. Rev.*, **77**, 792 (1950).
- [3] E. B. ROSA and G. W. VINAL: *Bull. U. S. N. Bur. Standards*, **13**, 479 (1916-17).
- [4] S. J. BATES: *Doctorate Thesis* (University of Illinois, 1912).
- [5] S. J. BATES and G. W. VINAL: *Journ. Am. Chem. Soc.*, **36**, No. 5, 916 (1914).
- [6] R. T. BIRGE: *Rev. Mod. Phys.*, **1**, 1 (1929).
- [7] R. T. BIRGE: *Reports on Progress in Physics (British)*, **8**, 114 (1942).
- [8] A. F. SCOTT: *U. S. Nat. Bur. Standards Circular 524. Electrochemical Constants*, Paper No. 1, 1 (1953).
- [9] D. N. CRAIG and J. I. HOFFMAN: *U. S. Nat. Bur. Standards Circular 524. Electrochemical Constants*, Paper No. 2, 13 (1953).
- [10] D. A. MACINNES: *U. S. Nat. Bur. Standards Circular 524, Electrochemical Constants*, discussion following Paper No. 2, 20 (1953).
- [11] M. SIEGBAHN: *Spektroskopie der Röntgenstrahlen* (Berlin, 1931).
- [12] A. H. COMPTON and S. K. ALLISON: *X-Rays in Theory and Experiment* (New York, 1934).
- [13] E. INGELSTAM: *Die K-Spektren der schweren Elemente*, Dissertation (Uppsala, 1937).
- [14] Y. CAUCHOIS and H. HULUBEI: *Longueurs d'Onde des Emissions X et des Discontinuités d'Absorption X* (Paris, 1947).
- [15] W. BRAGG: *Proc. Roy. Soc.*, A **88**, 428 (1913); A **89**, 246, 430 (1914).
- [16] A. H. COMPTON, H. N. BEETS and O. K. DEFoe: *Phys. Rev.*, **25**, 625 (1925).
- [17] E. BÄCKLIN: *Thesis* (Uppsala, 1928).
- [18] A. H. COMPTON and R. L. DOAN: *Proc. Nat. Acad. Sci. (U.S.)*, **11**, 598 (1926).
- [19] J. THIBAUD: *Journ. Phys. et Rad.*, **8**, 13, 447 (1927).
- [20] J. A. BEARDEN: *Phys. Rev.*, **37**, 1210 (1931); **48**, 385 (1935).
- [21] E. BÄCKLIN: *Zeits. f. Phys.*, **93**, 450 (1935).
- [22] M. SÖDERMAN: *Nature*, **135**, 67 (1935); *Dissertation* (Uppsala, 1934).
- [23] F. TYRÉN: *Zeits. f. Phys.*, **109**, 722 (1938).
- [24] R. T. BIRGE: *Amer. Journ. of Phys.*, **13**, 69 (1945).
- [25] J. A. BEARDEN: *Phys. Rev.*, **38**, 2089 (1931).
- [26] R. T. BIRGE: *Amer. Journ. Phys.*, **13**, 63 (1945).
- [27] E. M. PURCELL, H. C. TORREY and R. V. POUND: *Phys. Rev.*, **69**, 37 (1946); N. BLOEMBERGEN, E. M. PURCELL and R. V. POUND: *Phys. Rev.*, **73**, 679 (1948).
- [28] F. BLOCH: *Phys. Rev.*, **70**, 460 (1946); F. BLOCH, W. W. HANSEN and M. PACKARD: *Phys. Rev.*, **70**, 474 (1946).
- [29] H. A. THOMAS, R. L. DRISCOLL and J. A. HIPPLE: *Journ. Res. Nat. Bur. Standards*, **44**, 569 (1950); *Phys. Rev.*, **78**, 787 (1950).
- [30] N. F. RAMSEY: *Phys. Rev.*, **78**, 699 (1950).
- [31] H. A. THOMAS: *Phys. Rev.*, **80**, 901 (1950).
- [32] H. SOMMER, H. A. THOMAS and J. A. HIPPLE: *Phys. Rev.*, **82**, 697 (1951).

- [33] F. BLOCH and C. D. JEFFRIES: *Phys. Rev.*, **80**, 305 (1950).
- [34] C. D. JEFFRIES: *Phys. Rev.*, **81**, 1040 (1951).
- [35] D. J. COLLINGTON, A. N. DELLIS, J. H. SANDERS and K. C. TURBERFIELD: *Phys. Rev.*, **99**, 1622 (1955).
- [36] K. R. TRIGGER: Abstract UAS, Washington D. C. Meeting, *Bull. Amer. Phys. Soc.*, **1**, 220 (1956).
- [37] S. TRIEBWASSER, E. S. DAYHOFF and W. E. LAMB jr.: *Phys. Rev.*, **89**, 98 (1953); E. S. DAYHOFF, S. TRIEBWASSER and W. E. LAMB jr.: *Phys. Rev.*, **89**, 106 (1953).
- [38] W. E. LAMB jr. and R. C. RETHERFORD, (I): *Phys. Rev.*, **79**, 549 (1950).
- [39] W. E. LAMB jr. and R. C. RETHERFORD, (II): *Phys. Rev.*, **81**, 222 (1951).
- [40] W. E. LAMB jr., (III): *Phys. Rev.*, **85**, 259 (1952).
- [41] W. E. LAMB jr. and R. C. RETHERFORD, (IV): *Phys. Rev.*, **86**, 1014 (1952).
- [42] J. SCHWINGER: *Phys. Rev.*, **73**, 416 (1948).
- [43] R. KARPLUS and N. M. KROLL: *Phys. Rev.*, **81**, 73 (1951).
- [44] W. E. LAMB jr.: *Phys. Rev.*, **85**, 263 (1952), see Eq. (134).
- [45] E. R. COHEN: *Phys. Rev.*, **88**, 353 (1952).
- [46] J. W. M. DUMOND and V. L. BOLLMAN: *Phys. Rev.*, **51**, 400 (1937).
- [47] W. K. H. PANOFSKY, A. E. S. GREEN and J. W. M. DUMOND: *Phys. Rev.*, **62**, 214 (1942).
- [48] J. A. BEARDEN, F. T. JOHNSON and H. M. WATTS: *Phys. Rev.*, **81**, 70 (1951).
- [49] A. NILSSON: *Ark. f. Fys.*, **6**, No. 49, 544 (1953).
- [49a] W. M. DUMOND and E. R. COHEN, *Rev. Mod. Phys.*, **25**, 691 (1953).
- [50] C. W. LI, W. WHALING, W. FOWLER and C. C. LAURITSEN: *Phys. Rev.*, **83**, 512 (1951).
- [50a] E. R. COHEN and W. F. HORNYAK: *Phys. Rev.*, **72**, 1127 (1947); A. TOLLESTRUP, W. A. FOWLER and C. C. LAURITSEN: *Phys. Rev.*, **78**, 372 (1950).
- [51] D. M. VAN PATTTER and W. WHALING: *Rev. Mod. Phys.*, **26**, 402 (1954).
- [52] A. H. WAPSTRA: *Physica*, **21**, 367 (1955).
- [52a] J. E. DRUMMOND: *Phys. Rev.* **97**, 1004 (1955).
- [53] E. R. COHEN: *Phys. Rev.*, **88**, 353 (1952).
- [54] J. H. GARDNER and E. M. PURCELL: *Phys. Rev.*, **76**, 1262 (1949).
- [55] J. H. GARDNER: *Phys. Rev.*, **83**, 996 (1951).
- [56] H. SOMMER, H. A. THOMAS and J. A. HIPPLE: *Phys. Rev.*, **82**, 697 (1951).
- [57] W. V. HOUSTON: *Phys. Rev.*, **30**, 608 (1927).
- [58] J. W. DRINKWATER, O. RICHARDSON and W. E. WILLIAMS: *Proc. Roy. Soc.* **174**, 164 (1940).
- [59] D. Y. CHU: *Phys. Rev.*, **55**, 175 (1939).
- [60] S. H. KOENIG, A. G. PRODELL and P. KUSCH: *Phys. Rev.*, **88**, 191 (1952).
- [61] I. I. RABI, S. MILLMAN, P. KUSCH and J. R. ZACHARIAS: *Phys. Rev.*, **55**, 526 (1939).
- [62] R. BERINGER and M. A. HEALD: *Phys. Rev.*, **95**, 1474 (1954).
- [63] A. A. MICHELSON, F. G. PEASE and F. PEARSON: *Astrophys. Journ.*, **82**, 26 (1935).
- [64] W. C. ANDERSON: *Rev. Sci. Instr.*, **8**, 239 (1937); *Journ. Opt. Soc. Am.*, **31**, 187 (1941).
- [65] K. BOL: *Thesis* (Stanford University, 1950); *Phys. Rev.*, **80**, 298 (1950).
- [66] E. BERGSTRAND: *Nature*, **163**, 338 (1949); **165**, 405 (1950); *Ark. f. Fys.*, **2**, 119 (1950); **3**, 479 (1951).
- [67] I. C. C. MACKENZIE: *Ordnance Survey Professional Paper*, No. 19 (H. Maj. Stat. Off., London, 1954).
- [68] L. ESSEN: *Proc. Roy. Soc.*, A **204**, 260 (1950); *Nature*, **167**, 758 (1951).
- [69] K. D. FROOME: *Proc. Roy. Soc.*, A **213**, 123 (1952); A **223**, 195 (1954).
- [70] L. ESSEN and K. D. FROOME: *Nature*, **167**, 512 (1951).
- [71] L. ESSEN and K. D. FROOME: *Proc. Phys. Soc.*, B **64**, 862 (1951).

Mathematical Analysis of the Universal Physical Constants.

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In the previous paper Professor DuMOND has presented a wealth of experimental data on the universal physical constants (primarily those known as the atomic constants). This material is made up of a score or more individual experimental results. Not all of these are of equal experimental accuracy. Some of them may be combined among themselves to yield a simple datum which represents an average value of several independent evaluations of the same physical quantity. In whatever way this may be done we still find ourselves with more data than are required to obtain an evaluation of the fundamental physical constants. This may be expressed by a classical example (the example is classical in that it represents one of the first instances in which the existence of the overdetermined nature of the experimental data became forcefully evident.)

The value of the faraday constant as measured by the silver voltameter is [1] $F = Ne = 9651.29 \pm 0.19$ emu/mole; the atomic weight of the electron as inferred from the isotopic shift in the Balmer series for hydrogen and deuterium is [2] $Nm = (54.895 \pm 0.008) \cdot 10^{-8}$ amu. From this we can calculate a value for the specific electronic charge

$$e/m = (1.75814 \pm 0.00026) \cdot 10^7 \text{ emu/g}.$$

In comparison with this the value of e/m determined from measurements of the acceleration and deflection of electrons in electromagnetic fields yields a value [3]

$$e/m = (1.75959 \pm 0.00038) \cdot 10^7 \text{ emu/g}.$$

We could of course have equally well used the measured values of the atomic weight of the electron and the specific electronic charge to calculate an «indirect» value of the Faraday constant, or conversely use the specific electronic charge and the Faraday to find an indirect value of the electron's atomic weight. These calculations are summarized in Table I. We are then

TABLE I. — Comparison of direct and indirect values from a simple overdetermined system.

	$F = Ne$ (emu/mole)	Nm (amu)	e/m (emu/g)
Direct Values	$9\,651.29 \pm 0.19$	$(54.895 \pm 0.008) \cdot 10^{-5}$	$(1.759\,59 \pm 0.000\,36) \cdot 10^7$
	$(Nm)(e/m)$	$F/(e/m)$	F/Nm
Indirect Values	$9\,659.32 \pm 1.83$	54.849 ± 0.006	$1.758\,14 \pm 0.000\,26$

presented with the embarrassing problem of choosing which consistent set of three numbers ought to be used; each choice is certainly poor in itself since each is contradicted by the other two. It should be emphasized that the numbers presented in this table are illustrative and although based on direct measurements, do not represent in any way a selection of «best» data or are they to be considered as recommended numbers. They are presented in order to show the nature of the difficulty (which is actually compounded many-fold) when we attempt to analyze the experimental data on the atomic constants, considering these data as a single unified complex of experimental results. The experiments described in the preceding paper measure various combinations of the atomic constants. In some experiments the same combination or the same constant is measured in different ways; in others a measurement is made of a quantity whose value is also deducible from combining the results of two or more different and independent experiments. Thus we are confronted with an inter-related complex which is similar (in an abstract form) to the situation which is found most often in geodetic triangulation. Let us therefore look more closely at the structure of our present problem.

Each of the quantities whose measurement is described in the preceding paper can be expressed in terms of h , e , m , N , A , c , and a few other auxiliary quantities whose numerical values are accurately known. The Rydberg constant, however, which is a function of h , e , m , and c , is much more accurately measured than are any of its component factors. It is therefore convenient to consider the Rydberg constant as an exact numerical quantity and to use it to express the electron/mass as a known function of the other variables. In addition, to the accuracy required in the discussion to follow, it is convenient to treat the velocity of light, c , as an exactly known quantity. Furthermore,

because of the fact that the fine structure constant, α , is more accurately determined by direct observation of fine structure in hydrogen than it can be computed by combining, say measurements of e , h/e and c , it is also convenient to use α as a variable in place of h . Thus we shall choose to express all of the experimental results in terms of the quantities α , e , N , and A which we may call the primary unknowns of our analysis. The result of any experiment can then be described as measuring (except for quantities which can be considered as accurately calculable correction factors) some product of powers of the primary variables of the form

$$(1) \quad f(\alpha, e, N, A) = \alpha^a e^b N^c A^d = A(1 \pm \sigma).$$

The second expression is not actually an equation: it is a short-hand method for indicating that we do not know the true value of the right hand side of the equality but that the experiment can be interpreted as indicating a value which is defined only to the extent of a probability distribution with mean value A and with relative standard deviation σ . This interpretation is not the only one however and we shall discuss a different interpretation later.

For convenience in analyzing the data it is useful to linearize our equations. We adopt origin values α_0 , e_0 , N_0 , A_0 , which have been chosen sufficiently close to our expected solution that any set of values α , e , N , A (any point in our « constants-space ») in which we are likely to be interested will differ from the origin values by small amounts. « Small » is determined here by the magnitudes of the second derivatives of the function f ; we assume that we can expand $f(e, \alpha, N, A)$ as a multivariate Taylor series about the origin point, and that in such an expansion only the linear terms need be retained. It is in practice most convenient to expand the logarithm of f in a Taylor series; we then deal with relative deviations and if the function is a simple product of powers of the variables as is the case here, we obtain, in place by Equation (1), the linearized equation

$$(2) \quad ax_\alpha + bx_e + cx_N + dx_A = h \pm \sigma,$$

where $x_\alpha = (\alpha - \alpha_0)/\alpha_0$; $x_e = (e - e_0)/e_0$, etc., and $h = (A - A_0)/A_0$ in which A_0 is the value of the function f evaluated with the origin values α_0 , e_0 , N_0 , A_0 .

1. - A geometrical interpretation.

There are various ways in which we can interpret the experimental data geometrically. Professor BIRGE in his paper has discussed various types of diagrams [4-7] which he has used to aid him in evaluating « best » or « most

consistent » values of the atomic constants whose numerical magnitudes he seeks. These geometrical descriptions are all representations (in terms of various types of projections) of the following geometrical structure.

We may represent each experimental determination as defining a single functional relationship among the various physical constants. We may consider that an independent set of constants forms an orthogonal co-ordinate system in a « constants-space ». Each functional relationship (each experiment) then is represented by a surface in this space. An arbitrary point in the space (a given set of values of the constants, say α , e , N , A) is in agreement with the experimental result if it lies in the surface. A point (that is, a set of values for the constants) is therefore consistent with several experimental results if it lies at the common intersection of the surfaces. In general if we have more experiments (surfaces or equations) than we have constants to be determined (dimensionality of the space) it is not a priori evident that there will be a point through which *every* surface passes. If the experiments are reasonably consistent there will be a point, however, which is close to all of the surfaces. The best choice for the set of physical constants is that point which is « closest » to all of the surfaces. The definition of « distance » in this space (that is, the definition of a metric) we shall discuss below; for the moment let us *assume* that we can define distance. We should then want to consider a metric function defined with regard to the point in question and the existing surfaces. The problem we then set for ourselves is to find the point which minimizes this function.

This leads us to a second geometrical representation of the problem. At each point in our « constants-space » we have defined the value of a certain function. We now consider a space of one higher dimensionality and consider a hyper-surface whose distance from an orthogonal subspace (the original constants-space) is defined at each point by the value of a certain function (the exact form of this function we have not yet specified). We then seek the point on this surface which is a minimum. It is possible to make several general remarks about the form of the function, which we shall call Q . It must primarily be defined in such a way that its value is independent of the actual variables used to describe it. This means that Q is a scalar with respect to a transformation or rotation in the « constants-space ». In addition it should also be invariant with respect to non-essential modifications in the form in which the experimental results are presented. Again a simple example may be in order.

Let us suppose that one of our experimental equations can be written in the form

$$(3) \quad ax_1 + bx_2 + cx_3 = h \pm \sigma,$$

which states that the experimental result h was obtained with a standard

error $\pm \sigma$. If we transform variables from x_1, x_2, x_3 to a new set of variables y_1, y_2, y_3 , we obtain in place of this equation the expression

$$(3a) \quad \alpha y_1 + \beta y_2 + \gamma y_3 = h \pm \sigma.$$

The function Q must be defined in terms of the coefficients a, b, c , (and the corresponding coefficients of all of the other experimental data) in such a way that $Q(\alpha, \beta, \gamma; y_1, y_2, y_3)$ should be equal to $Q(a, b, c; x_1, x_2, x_3)$. Furthermore Q must be invariant with respect to transformation of the equations; the most easily recognized type of function transformation would be the replacement of equation (3) by the expression

$$(3b) \quad nax_1 + nbx_2 + ncx_3 = nh \pm n\sigma.$$

When this is done it is perhaps suggestive that all of the experimental equations ought to be written in a normalized form

$$(4) \quad \frac{a}{\sigma} x_1 + \frac{b}{\sigma} x_2 + \frac{c}{\sigma} x_3 = \frac{d}{\sigma} \pm 1.$$

When the equations are written in this form all of the equations have equal accuracy and we might then infer that they ought to be given equal weight in the analysis. At this point we use the word « weight » in a qualitative sense; later we shall give a quantitative definition which will formalize the intuitive notion that data with small standard errors should be given more weight or importance and data with larger errors should be given less weight in any analysis.

2. - The criterion of least squares.

Until now we have purposely made only very general statements about the problem of finding the best or most consistent set of unknowns from a set of overdetermined equations. It may perhaps be apparent that we would like to introduce the criterion of least squares in a logical and completely deductive manner. It is almost certain that this cannot be done; we can however carry our deductive development to a certain point, then inductively introduce the least squares criterion and finally justify the choice (at least partially) by considering the conditions which it must satisfy. We could specify that the function Q which has been previously mentioned shall be defined as the sum of the squares of the deviation of the point from each of

the experimentally defined surfaces, each deviation normalized by dividing it by the standard deviation of the experimental measurement. The condition that Q be a minimum is therefore the usual condition of «least squares» which was first formulated by GAUSS about 1820 [8].

There have been many who have objected to the use of the method of least squares on the grounds that it assumes the Gaussian curve for the probability distribution of the error in any particular measurement. The objection is indeed valid that the assumption of the Gaussian distribution is often unwarranted in many experimental configurations. The real problem at issue, however, is one of determining a «best» set of values that can be computed from an over-determined system of equations, and this is essentially the problem of determining an analytic basis on which one can define the adjective «best.» The condition of least squares serves as one such analytic criterion. This says nothing in itself of what could be called the physical interpretation of the criterion. It is recognized, in general, that the method of least squares corresponds to the «Axiom of Maximum Likelihood», if the distribution functions of all the errors are Gaussian [9]. GAUSS himself was able to justify the method on a much wider base, and in 1821 he published a theory which replaces this axiom with an «Axiom of Minimum Error» or «Axiom of Maximum Weight.» [10]. The definition of «best» is not to be made on the basis of that solution which is most likely to be correct, but on that combination of data which yields the most accurate result and to which can, therefore, be attached the greatest statistical weight. (The statistical weight of a statistical variable is defined in the present sense as the reciprocal of the variance, i.e., the reciprocal of the mean square error, of the quantity.) Consider then an overdetermined set of n equations expressing relationships between q variables. We can find an infinite number of solutions for the q variables depending on how we choose to combine the equations. We can think of this process as one in which some set of $q-1$ of the equations are used to express $q-1$ of the variables in terms of one particular variable, say x_1 . These values are then to be substituted into the remaining $n-q+1$ equations to give a set of $n-q+1$ values for the variable x_1 . Any of these numerical values is a possible choice for the variable x_1 and, in general we would want to take some weighted average of these numerical values. The numerical value of such an average depends both on the weights attached to the elements that go to make up the average and on the numerical values of these elements. Ultimately, therefore, the value ascribed to x_1 depends on $n-q$ independent and arbitrary parameters which specify the mathematical form of the average and n quantities which are either the observational numerics or quantities directly deduced from them (such as relative deviations from a set of origin values) which determine the numerical value of the average. There are only $n-q$ arbitrary parameters rather than $n-q+1$ because the

choice of the $n - q + 1$ weights is restricted by the condition that their sum is unity.

The numerical value of x_1 is thus expressed as a linear combination of n numerical quantities, each of which has associated with it a mean square error. If the numerical quantities are observationally independent, we can assert that the mean square error of x_1 is the sum of certain coefficients depending on the $n - q$ free parameters, times the mean square errors of the n observational numerics. The Axiom or Condition of Minimum Error states that the «best» choice for x_1 is that one whose error is a minimum with respect to the possible variation of the free parameters. This condition is equivalent to the condition of least squares, although the results cannot, in general, be identified as corresponding to that set which has maximum likelihood except in the case when the distribution function for the errors is specified to be Gaussian. This is however, an advantage for one can easily construct distributions (for example, rectangular distributions) for which the condition of maximum likelihood has no unique solution. Furthermore, the development of the condition of minimum error is quite general in regard to the forms of the error distribution functions; all that is specified is the mean square error, so that the range of applicability of the theory of least squares is extended from Gaussian distributions to the much larger class of distributions with finite second moments.

As an elementary example of the method and in order to clarify the concepts involved, let us consider a problem which is perhaps the simplest possible example. We have two measurements of the quantity x ; these two measurements are a_1 and a_2 , in general, $a_1 \neq a_2$. We also assume that each measurement represents a single selection from a universe of values. We let the probability distribution of the first measurement be $P_1(\xi)$ such that the probability is $P_1(\xi)d\xi$, that the result of a measurement of the quantity x by the specified procedure shall lie between the values ξ and $\xi + d\xi$. Similarly, the second measurement of x is to be characterized by the probability distribution $P_2(\eta)$. We need not make any detailed specification of the form of the distribution functions P_1 and P_2 ; it is not even necessary that the two functions have similar form. We impose upon them only the restriction that the distributions have finite second moments.

If we have two measurements of x then we can take some average value to use as the «best» choice. There are, however, several different choices for this average and we can write

$$(5) \quad x_0(\alpha) = \alpha a_1 + (1 - \alpha) a_2,$$

where α is any real number, although intuitively we would prefer that $0 < \alpha < 1$ because this is the condition that x_0 lies between the values a_1 and a_2 . Defined in this way, the mean of the universe of values of x_0 is

$$(6) \quad \bar{x}_0 = \iint [\alpha \xi + (1 - \alpha) \eta] P_1(\xi) P_2(\eta) d\xi d\eta.$$

Each probability distribution is assumed to be normalized and if there are no systematic errors in either measurement, the expectation value of each measurement is x .

Therefore we find

$$(7) \quad \bar{x}_0 = \alpha x + (1 - \alpha)x = x,$$

so that the expectation value of the average is indeed the quantity we are trying to measure, independent of the parameter α which determines the particular average. But we now ask the question: « How accurate is this average; what is its standard deviation? » If we let ε^2 be the mean square deviation of the universe from which x_0 is extracted, we have, by the usual definition,

$$(8) \quad \begin{aligned} \varepsilon^2 &= \iint [\alpha \xi + (1 - \alpha) \eta - x]^2 P_1(\xi) P_2(\eta) d\xi d\eta = \\ &= \alpha^2 \int (\xi - x)^2 P_1(\xi) d\xi + (1 - \alpha)^2 \int (\eta - x)^2 P_2(\eta) d\eta. \end{aligned}$$

The two integrals in the last form of Equation (8) are the variances (the mean square errors), respectively, of the first and of the second measurements. These quantities are defined to be σ_1^2 and σ_2^2 . The expression for the error in the average in terms of the errors of the numbers entering into the average is, therefore,

$$(9) \quad \varepsilon_0^2 = \alpha^2 \sigma_1^2 + (1 - \alpha)^2 \sigma_2^2.$$

We find that, although the expectation value of the average is independent of α , the error in the average is a function of α . For $\alpha = 0$ we have $\varepsilon^2 = \sigma_2^2$ and for $\alpha = 1$ we have $\varepsilon^2 = \sigma_1^2$; we may reasonably ask whether a proper choice of α might not result in a value of ε^2 which is smaller than either of these and indeed what value of α leads to a minimum value of ε^2 . It is easily shown that the minimum value of ε^2 is

$$(10) \quad \varepsilon_0^2 = \sigma_1^2 \sigma_2^2 / (\sigma_1^2 + \sigma_2^2)$$

which is achieved when $\alpha = \sigma_2^2 / (\sigma_1^2 + \sigma_2^2)$ and the corresponding value of x_0 is

$$(11) \quad x_0 = \varepsilon_0^2 \left[\frac{a_1}{\sigma_1^2} + \frac{a_2}{\sigma_2^2} \right].$$

We shall use Roman letters to indicate the indices which range from 1 to q and which refer to the unknowns, and Greek letters for those which range from 1 to n and refer to the observational equations.

Since the c_μ are assumed to be independent, the errors η_μ in c_μ are uncorrelated and

$$(14) \quad \begin{cases} \langle \eta_\mu \eta_\nu \rangle = \sigma_\mu^2 & \text{if } \nu = \mu, \\ = 0 & \text{if } \nu \neq \mu. \end{cases}$$

We wish to find x_i as a linear combination of the c with appropriate coefficients, λ_μ^i chosen so as to determine the x_i with maximum accuracy or minimum error. Thus we write

$$(15) \quad \begin{aligned} x_i &= \lambda_1^i c_1 + \lambda_2^i c_2 + \lambda_3^i c_3 + \dots + \lambda_n^i c_n \\ &= \sum_\mu \lambda_\mu^i c_\mu = \sum_{\mu j} \lambda_\mu^i a_{\mu j} x_j. \end{aligned}$$

This equation is to be understood as follows. Each of the n individual equations of observation (identified by the index μ) is to be multiplied by a number, λ_μ^i , there being a set of n such numbers for each variable x_i . These numbers are to be chosen such that, when the n equations are then summed, the coefficient of each x , other than the specified x_i , is zero, while the coefficient of x_i is unity. This implies that there are q conditions on each of the q sets of n multipliers. This is not sufficient to define the multipliers since $n > q$. The additional conditions are obtained by requiring that we choose that linear combination for each variable x_i which will have the smallest variance and hence the largest possible weight. It can be shown [11] that such a condition leads to exactly the same values of x_i as would be obtained from the condition that we minimize the quadratic form

$$(16) \quad Q = \sum_\mu \left(\frac{a_{\mu 1} x_1 + a_{\mu 2} x_2 + \dots + a_{\mu q} x_q - c_\mu}{\sigma_\mu} \right)^2.$$

Hence the condition of Minimum Error is just the least squares condition and is therefore equivalent to the condition of Maximum Likelihood of the more restricted Gaussian case. It is, however, much more general than the latter. No restriction is put on the probability distributions of the input errors, η_μ , in the c_μ other than that these distributions must have finite second moments, i.e., the σ_μ must exist. Subject to this condition, they may have more than one «mode» or indeed any arbitrary shape; nor is it necessary that the distribution functions all have the same form.

This generality of the significance of the least squares adjustment when stated in terms of the second moments of the error distribution is of great importance. It emphasizes also the desirability of adopting the root-mean-square deviation as a measure of error in preference to such error measures as the «probable error», or the «mean absolute error.» For a gaussian distribution, the three measures, root-mean-square error, mean absolute error and probable error (that error which divides the distribution curve into equal areas, so that the probabilities of errors of absolute magnitude greater than or less than the probable error are equal) stand in the ratios 1:0.798 0:0.674 5. It is however a mistake to think of the different error measures as simply expressing the same error spread on different scales. When we do not limit ourselves to gaussian distribution the root-mean-square error or standard error enjoys a position of far greater statistical significance and generality than do the others. This is because the standard deviation has a simple reproduction property (for any form of probability distribution) which is not shared by any other parameter with the same generality.

It may even be worthwhile to avoid the discussion of probability distributions and variances entirely and speak only of statistical weights and the weight to be assigned to each experimental number or to any number that results from arithmetic combinations of experimental data.

It can be shown, independently of the development which led to Equation (16) that if the weight to be assigned to a random variable is to be in accord with certain elementary axioms regarding the definition of weight and at the same time be a function only of the standard error of the variable, then that function is uniquely determined to be the reciprocal of the variance. The weight of a quantity should therefore be defined in such a way that it is consistent with the identification as the reciprocal of the variance in those cases where a variance can be experimentally determined. But we should be prepared as well to admit to consideration subjective evaluations of the weight of an experiment based on an impartial and honest appraisal of the inherent accuracy of one experiment in comparison to another even though no analytic evaluation of the variance exists. It may well be that the introduction of «weights» in place of «variances» is purely a semantic subterfuge; even so, it may prove a useful concept.

If, in equation (16), we introduce the notation

$$(17) \quad r_{\mu} = a_{\mu 1}x_1 + a_{\mu 2}x_2 + \dots + a_{\mu q}x_q - c_{\mu},$$

we can write Q in a matrix or tensor form [11, 12]

$$(18) \quad Q = r_{\mu} \tau_{\mu\nu} r_{\nu} = R^+ I R$$

in which $\pi_{\mu\nu}$ are the elements of a diagonal matrix

$$(19) \quad \begin{cases} \pi_{\mu\nu} = 1/\sigma_\mu^2 & \mu = \nu, \\ = 0 & \mu \neq \nu, \end{cases}$$

R is the vector with components r_μ and R^+ is the transposed vector. This form may appear cumbersome and unviably in actual use, and it is if the simpler formulation is available. However, it represents the point of departure for generalizing the formulation and establishing its complete invariance. If we perform a linear transformation on R and obtain $R' = TR$ we must write

$$(20) \quad Q = R'^+ T^{-1+} I T^{-1} R',$$

since Q must be a scalar invariant. Hence the transformed weight matrix I' is no longer diagonal. It now has the form

$$(21) \quad I' = T^{-1+} I T^{-1} = [T S T^+]^{-1},$$

where S is the inverse of the diagonal matrix I ; the diagonal elements of S are the variances σ_μ^2 . We see immediately however that the transformed matrix $S' = T S T^+$ is exactly the matrix which now expresses the variances and covariances of the transformed vector components r'_ν . The elements of S' are the mean error products, $\langle \eta'_\mu \eta'_\nu \rangle$. In the transformed system the errors η'_μ are not in general independent and hence S' is not diagonal as is the error matrix in equation (14). Thus, the form given in equation (18) represents the generalized statement of the least squares condition; the weight matrix I is the inverse of the error matrix, or covariance matrix, of the observational data. If the observational equations are not independent, the covariance matrix S and the weight matrix I are not diagonal. The off-diagonal elements of S are directly related to the degree to which the corresponding observational data are interdependent.

4. - Standard errors and correlation coefficients.

The statistical errors to be assigned to the output values of any least squares adjustment must, in general, be described not only by stating the standard deviation for each numerical result but also by specifying the correlations which exist between each pair of results. The numerical output values of α , e , N , etc., are of little use unless functions of these quantities can be com-

bined to compute other derived values. The standard deviations of such derived values must be computed by formulae which involve not only the standard deviations of the values entering into the function but also the covariances v_{ij} connecting all possible pairs of those values. This is because the output values of a least squares adjustment are not in general statistically independent quantities but are «statistically correlated».

Each quantity subject to random or accidental error (frequently known as a «random variable») may conveniently be thought of as a sample taken at random from a «universe» of values which group themselves around a mean value according to some frequency law. For each such random variable x_i , one is to think then of the implied universe of values from which the variable is selected. This universe may be described by giving some of its parameters. Thus, if the universe is known to be Gaussian, for example, then prescription of its first and second moments, i.e., its mean value, μ_i , and its variance σ_i^2 are sufficient.

Two such random quantities are observationally independent if the random selection of a sample value from one universe in no wise affects or biases the free selection of a sample from the other universe. If, for example, two variables are connected by a strict functional relationship so that the value of either one is uniquely determined by the other, the variables are completely correlated and the correlation coefficient connecting them has the absolute value unity. Random samples can no longer be selected freely and independently from the two universes because of the functional condition which ties the selections rigidly together. Having selected a sample value from one universe at random the second selection is now completely specified. On the other hand, if one of the two random variables is a function of the other and also of still other completely independent random variables, then these two will be partially but not completely correlated, and the correlation coefficient connecting them will have a value somewhere between -1 and $+1$. In general if we have a set of statistically independent random variables, y_μ , then a second set of variables, x_i , obtained by linear transformation on the y_μ

$$(22) \quad x_i = \sum_{\mu} \lambda_{i\mu} y_{\mu}$$

will not be statistically independent since a given one of the variables y_μ and hence a given source of error is present in more than one of the variables x_i . This of course is just the situation which exists in the problem of least squares adjustment. To each output value, x_i , there corresponds a standard deviation, σ_i , («variance» $v_{ii} = \sigma_i^2$) and to each pair (x_i, x_j) there corresponds a «covariance», $v_{ij} = r_{ij}\sigma_i\sigma_j$. The entire set of variances and covariances form a symmetric matrix which we may call the «error matrix.» The elements

of this matrix are required in order to compute the error measures of other quantities depending on the x_i .

5. — The standard errors of the residues of a least squares adjustment [13].

In any least squares adjustment of data it is obviously important to be able to assign a standard deviation to the difference between the adjusted output datum and the input datum from which it was obtained. Closely related to this question is the question of the value which would be obtained in a least squares analysis if a specific input datum had been omitted. The input and output data are certainly correlated and it would be incorrect to calculate the standard deviation of the difference without considering this correlation.

The measured input data consist of numbers c_μ as in equation (13); after the least squares solution has been performed and we have obtained the adjusted values for the x 's we can insert these values into equation (13) to obtain the adjusted value of c_μ which we shall designate by c_μ^* . The number c_μ^* is the best estimate which we can make of the correct value of c_μ based upon all the data available to us. The difference between c_μ and c_μ^* is thus a measure of the extent to which the observed value c_μ is consistent with all of the other data. In order to evaluate this consistency we must have an estimate of the magnitude of the difference which might be expected on the basis of statistical fluctuations. It can be shown fairly easily that the variance of the difference, $c_\mu - c_\mu^*$ is given by $\sigma_\mu^2 - \sigma_\mu^{*2}$ where σ_μ^2 is the variance of the input datum and σ_μ^{*2} is the variance of the adjusted value. This is a surprisingly simple result and it justifies the description of the adjusted value as being compounded of two terms; one is the direct input value c_μ while the other is an effective or indirect value which is determined by the combined action of all of the other data. This indirect value is the value of c_μ which would be deduced from a least squares analysis from which the directly observed datum had been omitted.

The indirect value and its variance are given by

$$(23) \quad c_\mu^i = \frac{\sigma_\mu^2 c_\mu^* - \sigma_\mu^{*2} c_\mu}{\sigma_\mu^2 - \sigma_\mu^{*2}} = c_\mu^* + \frac{\sigma_\mu^{*2}}{\sigma_\mu^2 - \sigma_\mu^{*2}} (c_\mu^* - c_\mu),$$

$$(24) \quad \sigma_\mu^{i2} = \frac{\sigma_\mu^2 \sigma_\mu^{*2}}{\sigma_\mu^2 - \sigma_\mu^{*2}}.$$

This expression for the variance implies that the statistical weights, which are proportional to the reciprocal of the variances are related by the equation

$$(25) \quad p_\mu^* = p_\mu^i + p_\mu, \quad p = C/\sigma^2.$$

If we use weights rather than variances, Equation (23) takes on the simple form

$$(26) \quad c_{\mu}^* = \frac{p_{\mu}c_{\mu} + p_{\mu}^i c_{\mu}^i}{p_{\mu} + p_{\mu}^i},$$

which is merely the statement that the least squares adjusted value is the weighted mean of the direct input value and the indirect value.

6. - Analysis of data.

We now at last come to the problem of making a specific analysis of a given set of experimental data in order to determine best values. We have formulated a procedure for doing this; we must now determine the data to which this procedure is to be applied. One must be especially careful not to apply the method of least squares blindly; it is not a substitute for careful selection of data. No provision exists in the method for identifying and isolating systematic error; the comparison of χ^2 with the theoretical probability table is useful in this regard but it is not definitive and can only indicate a probable existence of systematic error.

In a least squares fitting each datum is to be assigned a weight which is inversely proportional to its variance. Such a weighting is not arbitrary; it can be deduced directly from the form of the quadratic expression

$$Q = \sum (r_{\mu}/\sigma_{\mu})^2,$$

which we attempt to minimize. An observation with a large variance therefore carries little weight in determining the value of Q , and hence may be omitted without greatly affecting the result. There is, however, a more important reason for omitting data of low weight. When an experimenter designs his experiment he must carefully consider the possible presence of systematic error as well as the presence of random error. The random error of the final result can be reduced by duplication and repetition since these errors are different in each repetition; the systematic errors, on the other hand do not cancel out but remain. Now it is proper in an experiment to reduce any possible source of systematic error to a point where it may be of the order of, say, one tenth of the random error of a single observation. In this way the systematic error will be of the same order as, or smaller than, the random error of the final quoted result. However, it is neither feasible nor practical to do much better than this in the suppression of systematic error.

Thus an experiment with a quoted error which is large compared to another similar but more precise measurement may well be affected with a systematic

error which is large compared to the accuracy of the second experiment. This systematic error would then, a fortiori, be large compared to the accuracy which might be claimed for weighted mean of the two results. It would therefore be inappropriate to include the less precise observation in a weighted mean.

It is also necessary to reject data which suffer from serious systematic error even if (and perhaps, especially if) the data are precisely measured. Grounds for the suspicion of such systematic error may arise either from experimental sources (such as a reevaluation of the conditions under which the experiment was performed under such circumstances that corrections for such systematic errors can not be made to the existing data) or from theoretical sources (in which, as in the case of the hyperfine structure splitting in hydrogen the precision of the experiment is higher than the existing state of the theory of the experiment can handle).

By the first criterion for rejection mentioned above almost all of the historically important early experiments, including many which were considered important as late as 1947 are excluded. Within their estimated precision ranges such measurements are not inconsistent with the later more precise results but they are relatively so much less accurate as to have quite negligible influence in the present least squares adjustment. As a result of this criterion very few measurements published prior to 1950 remain.

Professor DUMOND has surveyed, in the previous paper, the important experiments which have a bearing on the values of the atomic constants. We shall now collect here those results which are to be used in an analysis of these constants.

(i) The *conversion factor* A , from the Siegbahn nominal scale of X-ray wavelengths (in X-units) to milliangstroms. We shall use the value recommended by Sir LAWRENCE BRAGG since it presumably supersedes the earlier value quoted by T. T. BIRGE (*):

$$(27) \quad A = 1.002\,020 \pm 0.000\,030.$$

(ii) The *Siegbahn-Avogadro number* N'_s . We use Birge's value converted to the physical scale

$$N'_s = NA^3 = (6.061\,79 \pm 0.000\,23) \cdot 10^{23} \text{ mole}^{-1}.$$

(iii) The *fine structure separation in deuterium*, ΔE_D : The frequency

(*) However, very recent information concerning TYRÉN's measurements on X-ray wavelengths indicates that this work suffers a systematic error of the order of 30 to 50 ppm because of the omission of the Lamb shift in the calibration of the photographic plates. (See the previous paper by J. W. M. DUMOND).

separation between the levels $2^2P_{\frac{3}{2}}$ and $2^2P_{\frac{1}{2}}$ measured by DAYHOFF, TRIEBWASSER and LAMB

$$(29) \quad \Delta E_D = \frac{1}{16} \alpha^2 R_D c \left(1 + \frac{5}{8} \alpha^2 \right) \left[1 + \frac{\alpha}{\pi} - 5.946 \frac{\alpha^2}{\pi^2} \right] = (110\,971.59 \pm 0.10) \text{ MHz}.$$

(iv) The *gyromagnetic ratio of the proton*, γ_p , obtained at the National Bureau of Standards by THOMAS, DRISCOLL and HIPPLE

$$(30) \quad \gamma_p = \mu' Ne / M_p c = (26\,725.3 \pm 0.3) \text{ s}^{-1} \text{ gauss}^{-1}.$$

(v) The determination of the *faraday* by electrolysis; although more accurate values may soon be available we are at the moment confronted with two somewhat discrepant measurements on silver and on iodine. The iodine value is

$$(31) \quad F = Ne/c = (9\,652.15 \pm 0.13) \text{ emu/mole} \quad (\text{physical scale}),$$

and the silver is

$$(32) \quad F = Ne/c = (9\,651.29 \pm 0.19) \text{ emu/mole} \quad (\text{physical scale}).$$

(vi) The *magnetic moment of the proton* in terms of the nuclear magneton. BLOCH and JEFFRIES obtain the value (uncorrected for diamagnetism)

$$(33) \quad \mu' = 2.792\,36 \pm 0.000\,10$$

and HIPPLE, SOMMER and THOMAS obtain for the same quantity

$$(34) \quad \mu' = 2.792\,68 \pm 0.000\,03.$$

(vii) The *short wavelength limit* of the continuous X-ray spectrum is unfortunately not known experimentally with sufficient accuracy to carry much weight in a least squares fitting. The difficulties here have been previously discussed [14]. It appears that the best experimental value is

$$(35) \quad hc^2/eA = (12\,370.8 \pm 1.0) \text{ emu}.$$

In formulating the data on which our input equations of observation are to be based, care had been taken to do so in such a way as to avoid hidden correlations between the equations of observation. For example, the measurements resulting from observed values of crystal densities and their X-ray grating constants are almost invariably quoted as measurements of Avogadro's

number, N . To obtain N from these measurements, however, it is necessary to combine the results with the cube of the conversion constant, A . Consequently we have equated the numeric which was actually measured to the appropriate function, $N \cdot A^3$, of our primary unknown. In other words we have been careful to see that no single measured quantity shall be involved as a substantial contributor to the error measures to two or more of the observational equations at once.

It will not be possible here to discuss the numerical details of the actual least squares analysis. These may be found elsewhere in the literature [15, 16]. Only the results and their evaluation will be presented. It has already been mentioned, probably more than once, that the experimental data are not entirely self-consistent. Thus, the two determinations of the Faraday constants (by iodine and silver voltameters) differ by 89 parts per million although each measurement claims to have an accuracy of 20 parts per million or better. The measurement of the proton magnetic moment by BLOCH and JEFFRIES is 115 parts per million higher than the measurement by HIPPLE, SOMMER and THOMAS. This is some three times larger than the standard deviation of the data would imply. The recently published reanalysis of this experiment [17] has resulted in a reduction of BLOCH and JEFFRIES' result by 109 parts per million, thus bringing it in excellent accord with HIPPLE, SOMMER and THOMAS. Furthermore, the modification of the inverse cyclotron by COLLINGTON, DELLIS, SANDERS and TURBERFIELD [18] yields a value which differs from TRIGGER's corrected BLOCH and JEFFRIES result by 21 ± 39 parts per million, and from HIPPLE, SOMMER and THOMAS omegatron value by 16 ± 18 parts per million. Professor DUMOND has already fully described the problems associated with the short wavelength limit.

A preliminary least squares analysis was carried out in 1952 with the data then available. This comprised thirteen equations in five variables, α , e , N , A and c . The value χ^2 (which is the minimum value of the function Q — the function whose minimization it is our object to obtain) was 52.1. This is a disturbingly large figure since there are only eight degrees of freedom and hence we would expect χ^2 to have the mean value 8 and to lie between the limits 2.73 and 15.51 with 90% confidence. The probability is less than one in a thousand that χ^2 would be larger than 26.1 entirely as a result of random error. We may say with almost complete certainty that there is a systematic error either in the observational data themselves or in the assignment of weights to those measurements.

The most convenient method for investigating the existence of systematic error in a set of data such as the one at hand is the comparison of the direct and indirect values of each input numeric as has been described earlier. Such a comparison was made and the implications are direct and conclusive [13]. The iodine value of the faraday for example is much more consistent with

the indirect value than is the silver faraday. The difference between the iodine value and the indirect value is 53 ± 26 parts per million, while the silver faraday differs from the indirect value by 142 ± 30 parts per million. The existence of sources of experimental systematic error in this measurement has been pointed out and this physical evidence strengthens the significance of the statistical implication.

Similarly the indirect value of the proton magnetic moment agrees with HIPPLE, SOMMER and THOMAS' value, thus indicating the possible existence of an error in the original inverse cyclotron work. This, of course, was later confirmed by TRIGGER's reanalysis [17] and the modified experiment carried out at Oxford by SANDERS *et al.* [18].

The determinations of the short wavelength limit of the continuous X-ray spectrum are all in disagreement with the indirect value. Hence we may tend to doubt the direct data; there are certainly valid experimental reasons why we should, and one is tempted to reject all of these data.

A word of caution is in order at this point. Of the thirteen items which were included in this preliminary analysis we have deduced reasons to reject five. This represents a rather drastic censoring and should be carried out with care. As soon as we eliminate one item the values of all of the other adjusted output values change. Hence strictly we should re-evaluate the least squares solution after each rejection in order to determine a new basis for the subsequent rejections. Furthermore, the decision to reject a datum as discrepant may very well depend upon the order in which other data are rejected. It is quite possible, in general, that a particular experimental result is in disagreement with the indirectly determined value, not because of an error in the experiment itself, but because some other error-ridden experiment is strongly distorting the indirect value. If the latter experiment were rejected first, the former one might well be retained. This is particularly liable to occur if the total degrees of freedom of the system is small so that each experimental item can contribute significantly to the overall result.

A completely different approach to the problem of determining which equations of the thirteen are likely to suffer from systematic error is afforded by an analysis of variance approach. This analysis involves the calculation of χ^2 for every possible subset of the thirteen equations and the comparison of these values of χ^2 to determine whether the value of 52.1 can be ascribed to the effect of one or a few items or whether all of the data contribute equally to this large value. In the first instance we would be willing to say that those items responsible for anomalously large contributions to χ^2 were, in fact, suffering from systematic error; in the second instance we would ascribe an increased standard error to all of the data and admit that if systematic errors existed they were so wide-spread as to defy unique identification.

A partial survey, although not complete, is adequate to confirm the implications of Table II: Silver coulometer value for the faraday constant and Bloch and Jeffries proton magnetic moment determination are in error and all of the short wavelength limit measurements are somewhat suspect. Actually suspicion does not fall strongly on the Bearden and Schwarz value but this is due more to its low weight than to its close agreement. Thus although its residue is in most comparisons as large or larger than the residues of the other

 TABLE II. — *Direct and indirect evaluation of fundamental constants (1952 Adjustment).*

Constant	Direct value (experimental)	Indirect value	Least squares solution	Residue of least squares solution (ppm)
1	$1.002\,020 \pm 0.000\,030$	$1.002\,073 \pm 0.000\,015$	$1.0020\,63 \pm 0.000\,013$	43 ± 27
$N \cdot 10^3$	$6\,061.79 \pm 0.23 \cdot 10^{20}$	$6\,062.90 \pm 0.39$	$6\,062.08 \pm 0.20$	48 ± 19
γ	$(26\,752.3 \pm 0.6) \text{ emu}^{-1} \text{ s}^{-1}$	$26\,751.9 \pm 0.4$	$26\,752.0 \pm 0.5$	-11 ± 20
F	(I) $(9\,652.15 \pm 0.13) \text{ emu/mole}$	$9\,651.90 \pm 0.15$	$9\,652.01 \pm 0.10$	-11 ± 9
	(Ag) $(9\,651.29 \pm 0.19) \text{ emu/mole}$	$9\,652.21 \pm 0.11$	$9\,652.01 \pm 0.10$	78 ± 17
μ'	(BJ) 2.79237 ± 0.00010	2.79270 ± 0.00005	2.79267 ± 0.00003	109 ± 34
	(HST) 2.79268 ± 0.00003	2.79263 ± 0.00005	2.79267 ± 0.00003	-5 ± 6
X-ray S.W.L.	(FHD) $(12\,370.02 \pm 0.63) \text{ emu cm}$	$12\,372.40 \pm 0.17$	$12\,372.23 \pm 0.16$	179 ± 48
	(BJW) $(12\,371.03 \pm 0.48) \text{ emu cm}$	$12\,372.37 \pm 0.17$	$12\,372.23 \pm 0.16$	97 ± 39
	(BS) $(12\,370.77 \pm 1.03) \text{ emu cm}$	$12\,372.28 \pm 0.17$	$12\,372.23 \pm 0.16$	119 ± 81

Remarks. — BJ = F. BLOCH and C. D. JEFFRIES; HST = J. A. HIPPLE, H. SUMMER and H. A. THOMAS; FHD = G. F. FELT, J. N. HARRIS and J. W. M. DuMOND; BJW = J. A. BEARDEN, F. T. JOHNSON and H. M. WATTS; BS = J. A. BEARDEN and G. SCHWARZ.

X-ray S.W.L. = Short wavelength limit of the continuous X-ray spectrum.

The column marked « Direct value » gives the experimental datum measured in the experiment which is indicated in the first column. The « Indirect value » is the one which would be deduced from a least squares analysis if the given experiment were excluded from consideration. If the same experiment is repeated by different observers only the single experiment in question (and not the others of the same kind) is excluded. The column marked « Residue of least squares solution » is the adjusted value of the 1952 analysis. The last column gives, in parts per million, the difference between the least squares solution and the input datum. The error quoted is the standard error of that difference.

[The fine structure splitting, ΔE_d , and the velocity of light have been omitted from this table because the direct measurements of these items have so much more weight than the indirect values that the elimination of numerical accuracy in the calculation precludes a meaningful evaluation of the latter].

short wavelength limit determinations, its contribution to χ^2 is much smaller because of the much larger standard error assigned to it.

The 1955 evaluation of the atomic constant [16] therefore rejected the silver faraday and BLOCH and JEFFRIES proton magnetic moment measurement. In addition the short wavelength limit values were replaced by a single expression based on the average of all the low voltage data as has been previously mentioned. It was also considered adequate to consider the velocity of light to be an auxiliary constant, not subject to least squares analysis. This rather drastic censoring of the data reduces the system to seven equations in four unknowns. The calculated value of χ^2 is then found to be 3.25 which is deceptively close to the expectation value, since the 90% confidence limits are $0.35 < \chi^2 < 7.81$. It can also be argued that the short wavelength limit measurements should be dropped entirely (and a strict adherence to our selection conditions would require this). In this case we decrease our system to one with only two degrees of freedom. The value of χ^2 is then only 0.44. This is at first sight quite low compared with the expectation value of 2.00; however the 90% confidence limits are 0.10 and 5.99. In fact, the probability that χ^2 might be lower than 0.44 is almost 20%, and this probability is further increased if we recognize that we have rather drastically censored all those data which contribute to large values of χ^2 . Furthermore, the actual solution is not greatly changed by rejecting the short wavelength limit data entirely; the largest change in any output value is less than one fourth of the assigned standard deviation.

The system of seven equations in four unknowns which is obtained when we exclude those data which appear to be discordant with the remainder of our data is given below. As has been mentioned above we assume the velocity of light to be an exact constant in this analysis, its value being

$$(36) \quad c = 299793.0 \text{ km/s.}$$

(The actual standard deviation to be assigned to this number is ± 0.3 km/s, but this error has a negligible effect on the numerical results of the least squares analysis.)

The origin values and the linearized variables are taken to be:

$$(37) \quad x_1 = \frac{\alpha - \alpha_0}{\alpha_0} \cdot 10^5 \quad \alpha_0 = 0.007297000,$$

$$(38) \quad x_2 = \frac{c - c_0}{c_0} \cdot 10^5 \quad c_0 = 4.802200 \cdot 10^{-10} \text{ esu},$$

$$(39) \quad x_3 = \frac{N - N_0}{N_0} \cdot 10^5 \quad N_0 = 0.6025000 \cdot 10^{24} \text{ mole}^{-1},$$

$$(40) \quad x_4 = \frac{A - A_0}{A_0} \cdot 10^5 \quad A_0 = 1.0020200.$$

With these definitions the observational equations become:

			Weight	Experimental source
(41)	$x_4 =$	0.0	0.11,	$A = 1.002\ 02 \pm 0.000\ 03$
(42)	$x_3 + 3x_4 =$	3.5	0.07,	NA^3 (Birge's average)
(43)	$x_1 =$	4.0	4.92,	Fine structure splitting in deuterium
(44)	$3x_1 - x_2 = -$	2.3	0.19,	Gyromagnetic ratio of proton
(45)	$x_2 + x_3 =$	11.1	0.58,	Iodine faraday, electrochemistry
(46)	$-3x_1 + 2x_2 + x_3 =$	13.5	0.83,	Magnetic moment of proton (omegatron)
(47)	$-x_1 + x_2 - x_4 = -$	5.6	0.015,	Short wavelength limit (low voltage)

The normal equations are formed according to the usual rules; they are

$$(48) \quad \begin{cases} (x) & 14.115x_1 - 5.565x_2 - 2.490x_3 + 0.015x_4 = -15.162 \\ (e) & -5.565x_1 + 4.105x_2 + 2.240x_3 - 0.015x_4 = 29.201 \\ (N) & -2.490x_1 + 2.240x_2 + 1.480x_3 + 0.210x_4 = 17.888 \\ (A) & 0.015x_1 - 0.015x_2 + 0.210x_3 + 0.755x_4 = 0.819 \end{cases}$$

It should be noted here that the normal equations are to be formed directly from the coefficients of the quadratic form, Q , as given in equation (16) and that no simplification or cancellation should be made in the equations. This is because the coefficients of the normal equations have a significance which is not limited to the determination of the values of the x_i . An alteration in the equations which would not alter the solution (such as the cancellation of a common factor in one of the equations, or even the re-ordering of the equations in the set) can destroy the identifications of the coefficients of the normal equations as the weight matrix of the solution.

The error (or variance) matrix of the solution is the inverse of the matrix of the coefficients of the normal equations. Hence the error matrix is

$$(49) \quad V = \begin{pmatrix} 0.198\ 9 & -0.576\ 0 & 0.560\ 3 & 0.163\ 3 \\ 0.576\ 0 & 3.447\ 8 & -4.431\ 9 & 1.289\ 8 \\ -0.560\ 3 & -4.431\ 9 & 6.716\ 7 & -1.945\ 2 \\ 0.163\ 3 & 1.289\ 8 & -1.945\ 2 & 1.887\ 9 \end{pmatrix} \begin{matrix} \alpha \\ e \\ N \\ A \end{matrix}$$

and the solution for the variables is

$$(50) \quad \begin{cases} x_1 = 3.92 \\ x_2 = 13.72 \\ x_3 = -2.37 \\ x_4 = 1.94 \end{cases}$$

The value of χ^2 for this solution is

$$(51) \quad \chi^2 = 3.25.$$

This is to be compared to the value 52.1 which was obtained in the preliminary adjustment. The major change in the variables caused by the deletion of those data suspected of systematic error is an increase in x_3 of 2.23 and an attendant decrease in x_4 of 2.35; this corresponds to a change in Avogadro's number N of 22.3 ppm and a change in the conversion factor A of -23.5 ppm.

The value of χ^2 can be expressed equivalently in terms of the ratio of external to internal consistency

$$r_e/r_i = \sqrt{\chi^2/(n-q)} = 1.041.$$

The 90% confidence interval for r_e/r_i with 3 degrees of freedom is $0.594 < r_e/r_i < 2.795$. Hence there is no particular compulsion to use internal rather than external consistency measures; our data tell us only that the two measures are consistent. We shall, however, quote our final error matrix in terms of external consistency since this is the larger measure (albeit not significantly so). Furthermore, the error matrix will be re-expressed in terms of relative parts per million in the primary variables.

The error matrix and correlation coefficients are given in Tables III and IV.

TABLE III. — *Covariance matrix (1955 Adjustment).*

Elements of the matrix are in units of (relative parts per million)².

	e	m	h	α	A	N	F
e	374	560	685	62	140	—480	—107
m	560	940	1057	60	226	—778	—218
h	685	1057	1246	103	262	—899	—216
α	62	60	103	22	18	—61	2
A	140	226	262	18	204	—211	—71
N	—480	—778	—899	—61	—211	726	246
F	—107	—218	—216	2	—71	246	141

TABLE IV. — *Correlation coefficients (1955 Adjustment).*

	<i>e</i>	<i>m</i>	<i>h</i>	α	<i>A</i>	<i>N</i>	<i>F</i>
<i>e</i>	1.00	0.95	0.99	0.70	0.51	— 0.92	— 0.47
<i>m</i>	0.95	1.00	0.97	0.43	0.52	— 0.94	— 0.60
<i>h</i>	0.99	0.97	1.00	0.63	0.52	— 0.94	— 0.51
α	0.70	0.43	0.63	1.00	0.27	— 0.48	0.03
<i>A</i>	0.51	0.52	0.52	0.27	1.00	— 0.55	— 0.42
<i>N</i>	— 0.92	— 0.94	— 0.94	— 0.48	— 0.55	1.00	0.77
<i>F</i>	— 0.47	— 0.60	— 0.51	0.03	— 0.42	0.77	1.00

The error matrix of Table III has been extended to include the variables *m*, *h* and *F*. These variables were eliminated from the least squares solution by the use of auxiliary equations. It is, however, inconvenient to be forced to use these equations in order to express *m*, *h* or *F* in terms of our primary variables each time one needs to compute correlation coefficients between these variables and other variables. The variances and correlation coefficients for these secondary variables can be calculated in terms of the variance matrix of the primary variables. Thus, although we have produced a matrix of seventh order it is still only of the fourth rank since three of the rows (or columns) can be expressed as linear combinations of the other rows (or columns). The near equality of *m* and *h* columns of the matrix of correlation coefficients (Table IV) is a reflection of the strong coupling between the adjusted values of these two variables.

This is a result of the relationship

$$m = \frac{2R_{\infty}h}{c\alpha^2},$$

and the fact that the relative standard error of α is much smaller than the error in either *m* or *h*.

7. — Output values. Recommended (1955) least squares adjustment.

The 1955 adjustment is based, as has been explained earlier, on the determination of four primary unknowns α , *e*, *N* and *A*, by least-squares adjustment from seven independent sources of experimental input data combined with a number of auxiliary constants whose values are known so much more accurately than the aforementioned input data that they are negligible error contributors.

The physical scale of atomic weights is used almost exclusively in these tables, the Sackur-Tetrode constant (given on both physical and chemical scales) being the sole exception. The conversion factor between these scales, $r = 1.000\,272 + 0.000\,005$ calculated by R. T. BIRGE on the basis of the abun-

dance ratio for the oxygen isotopes, $^{16}\text{O}:^{18}\text{O}:^{17}\text{O} = (506 \pm 10):1:(0.204 \pm 0.008)$ is adopted here as a definition for the chemical scale. These abundance ratios, and the value of r implied by them, are subject to variation depending on the source of the oxygen. The value of the $^{16}\text{O}/^{18}\text{O}$ ratio can vary from approximately 495 for oxygen from air or carbonates to 515 for oxygen from water and rocks. Corresponding to this variation is a variation in the value of r from 1.00278 to 1.00268. The International Commission on Atomic Weights is at present (1956) considering the arbitrary redefinition of the chemical scale of atomic weights in terms of the physical scale and the value $r = 1.00275$. The accuracy ascribed to our adopted value is such that these two numbers do not differ significantly (approximately one half the standard error).

The new Kelvin scale of temperature adopted October 1954 in Paris at the Tenth General Conference on Weights and Measures is here used. On this scale the triple point of water is assigned the temperature 273.16°K exactly. This changes the numerical value of the gas constant, R_0 , slightly from that used in earlier evaluations and gives the value of the ice point as $(273.1500 \pm 0.0002)^\circ\text{K}$. Absolute electrical units are used exclusively, the « international » electrical units having been abolished in 1948.

TABLE V. — *Auxiliary constants.*

Rydberg wave number for infinite mass

$$R_\infty = (109\,737.309 \pm 0.012) \text{ cm}^{-1}$$

Rydberg wave numbers for the light nuclei

$$R_{\text{H}} = (109\,677.576 \pm 0.012) \text{ cm}^{-1}$$

$$R_{\text{D}} = (109\,707.419 \pm 0.012) \text{ cm}^{-1}$$

$$R_{^{3}\text{He}} = (109\,717.345 \pm 0.012) \text{ cm}^{-1}$$

$$R_{^{4}\text{He}} = (109\,722.267 \pm 0.012) \text{ cm}^{-1}$$

Velocity of light

$$c = (299\,793.0 \pm 0.3) \text{ km s}^{-1}$$

Atomic mass of neutron

$$M_{\text{n}} = 1.008982 \pm 0.000003 \text{ (physical scale)}$$

Atomic mass of hydrogen

$$\text{H} = 1.008142 \pm 0.000003 \text{ (physical scale)}$$

Atomic mass ratio of hydrogen to proton

$$\text{H}/M_{\text{p}} = 1.00054461 \quad (\text{computed using atomic mass of electron } Nm = 0.00054875) \text{ (physical scale)}$$

Atomic mass of the proton

$$M_{\text{p}} = 1.007593 \pm 0.000003 \text{ (physical scale)}$$

Atomic mass of deuterium

$$\text{D} = 2.014735 \pm 0.000006 \text{ (physical scale)}$$

TABLE V: *continued.*

Atomic mass ratio of deuterium to deuteron

$$D/M_d = 1.000\,272\,44 \text{ (computed using atomic mass of electron, } Nm = 0.000\,548\,75 \text{ (physical scale))}.$$

Ratio of electron magnetic moment to proton magnetic moment without diamagnetic correction

$$[M_p/(Nm\mu')](1 + \alpha/2\pi - 2.973\alpha^2/\pi^2) = 658.228\,8 + 0.000\,4$$

Anomalous magnetic moment of electron

$$\mu_e/\mu_0 = (1 + \alpha/2\pi - 2.973\alpha^2/\pi^2) = 1.001\,145\,36$$

(computed using the value $1/\alpha = 137.037$)

Gas constant per mole

$$R_0 = (8.316\,96 \pm 0.000\,34) \cdot 10^7 \text{ erg mole}^{-1} \text{ deg}^{-1} \text{ (physical scale)}$$

Standard volume of a perfect gas

$$V_0 = (22\,420.7 \pm 0.6) \text{ cm}^3 \text{ atm mole}^{-1} \text{ (physical scale)}$$

 TABLE VI. - *Least squares adjusted output values, 1955.*

The quantity following each \pm sign is the standard error. Attention is called to the fact that the quantities in this Table are observationally correlated so that in the computation of the error measures of derived values dependent on two or more of the values in this Table the error matrix of Table III must be used.

Avogadro's constant

$$N = (6.024\,86 \pm 0.000\,16) \cdot 10^{23} \text{ mole}^{-1} \text{ (physical scale)}$$

Loschmidt's constant

$$L_0 = N/V_0 = (2.687\,19 \pm 0.000\,10) \cdot 10^{19} \text{ cm}^{-3} \text{ (physical scale)}$$

Electronic charge

$$e = (4.802\,86 \pm 0.000\,09) \cdot 10^{-10} \text{ esu}$$

$$e' = e/c = (1.602\,06 \pm 0.000\,03) \cdot 10^{-20} \text{ emu}$$

Electron rest mass

$$m = (9.108\,3 \pm 0.000\,3) \cdot 10^{-28} \text{ g}$$

Proton rest mass

$$m_p = M_p/N = (1.672\,39 \pm 0.000\,04) \cdot 10^{24} \text{ g}$$

Neutron rest mass

$$m_n = M_n/N = (1.674\,70 \pm 0.000\,04) \cdot 10^{24} \text{ g}$$

Planck's constant

$$h = (6.625\,17 \pm 0.000\,23) \cdot 10^{-27} \text{ erg s}$$

$$h/2\pi = (1.054\,43 \pm 0.000\,04) \cdot 10^{-27} \text{ erg s}$$

Conversion factor from Siegbahn X-units to milliangstroms

$$A = \lambda_g/\lambda_s = 1.002\,039 \pm 0.000\,014$$

TABLE VI: *continued.*

Faraday constant

$$F = Ne = (2.893\,66 \pm 0.000\,03) \cdot 10^{14} \text{ esu mole}^{-1}$$

$$F' = Ne/c = (9\,652.19 \pm 0.11) \text{ emu mole}^{-1} \quad (\text{physical scale})$$

Charge-to-mass ratio of the electron

$$e/m = (5.273\,05 \pm 0.000\,07) \cdot 10^{17} \text{ esu g}^{-1}$$

$$e/mc = (1.758\,90 \pm 0.000\,02) \cdot 10^7 \text{ emu g}^{-1}$$

Ratio h/e

$$h/e = (1.379\,42 \pm 0.000\,02) \cdot 10^{-17} \text{ erg s esu}^{-1}$$

Fine structure constant

$$\alpha = e^2/\hbar c = (7.297\,29 \pm 0.000\,03) \cdot 10^{-3}$$

$$1/\alpha = 137.037\,3 \pm 0.000\,6$$

$$\alpha/2\pi = (1.161\,398 \pm 0.000\,005) \cdot 10^{-3}$$

$$\alpha^2 = (5.325\,04 \pm 0.000\,05) \cdot 10^{-5}$$

$$1 - (1 - \alpha^2)^{\frac{1}{2}} = (0.266\,252 \pm 0.000\,002) \cdot 10^{-4}$$

Atomic mass of the electron

$$Nm = (5.487\,63 \pm 0.000\,06) \cdot 10^{-4} \quad (\text{physical scale})$$

Ratio of mass of hydrogen to mass of proton (*)

$$H/M_p = \left[1 - \frac{Nm}{H} \left(1 - \frac{1}{2} \alpha^2 \right) \right]^{-1} =$$

$$= 1.000\,544\,613 \pm 0.000\,000\,006$$

Atomic mass of proton

$$M_p = H - Nm = 1.007593 \pm 0.000003 \quad (\text{physical scale})$$

Ratio proton mass to electron mass

$$M_p/(Nm) = 1836.12 \pm 0.02$$

Reduced mass of electron in hydrogen atom

$$\mu = m M_p / H = (9.103\,4 \pm 0.000\,3) \cdot 10^{-28} \text{ g}$$

Schrödinger constant for a fixed nucleus

$$2m/\hbar^2 = (1.638\,36 \pm 0.000\,07) \cdot 10^{27} \text{ erg}^{-1} \text{ cm}^{-2}$$

Schrödinger constant for the hydrogen atom

$$2\mu/\hbar^2 = (1.637\,48 \pm 0.000\,07) \cdot 10^{27} \text{ erg}^{-1} \text{ cm}^{-2}$$

First Bohr radius

$$a_0 = \hbar^2/(me^2) = \alpha/(4\pi R_\infty) =$$

$$= (5.291\,72 \pm 0.000\,02) \cdot 10^{-9} \text{ cm}$$

Radius of electron orbit in normal ^1H , referred to center of mass

$$a'_0 = a_0(1 - \alpha^2)^{\frac{1}{2}} = (5.291\,58 \pm 0.000\,02) \cdot 10^{-9} \text{ cm}$$

Separation of proton and electron in normal ^1H

$$a''_0 = a'_0 R_\infty / R_H = (5.294\,46 \pm 0.000\,02) \cdot 10^{-9} \text{ cm}$$

(*) The binding energy of the electron in the hydrogen atom has been included in the quantity. The mass of the electron when found in the hydrogen atom is not m , but more correctly $m(1 - 1/2\alpha^2 + \dots)$.

TABLE VI: *continued.*

Compton wavelength of the electron

$$\lambda_{C,e} = \hbar/(mc) = \alpha^2/2R_\infty = (24.262\,6 \pm 0.000\,2) \cdot 10^{-11} \text{ cm}$$

$$\lambda_{C,e} = \lambda_{C,e}/2\pi = (3.861\,51 \pm 0.000\,04) \cdot 10^{-11} \text{ cm}$$

Compton wavelength of the proton

$$\lambda_{C,p} = \hbar/m_p c = (13.214\,1 \pm 0.000\,2) \cdot 10^{-14} \text{ cm}$$

$$\lambda_{C,p} = \lambda_{C,p}/2\pi = (2.103\,08 \pm 0.000\,03) \cdot 10^{-14} \text{ cm}$$

Compton wavelength of the neutron

$$\lambda_{C,n} = \hbar/m_n c = (13.195\,9 \pm 0.000\,2) \cdot 10^{-14} \text{ cm}$$

$$\lambda_{C,n} = \lambda_{C,n}/2\pi = (2.100\,19 \pm 0.000\,03) \cdot 10^{-14} \text{ cm}$$

Classical electron radius

$$r_0 = e^2/(mc^2) = \alpha^2/(4\pi R_\infty) =$$

$$= (2.817\,85 \pm 0.000\,04) \cdot 10^{-13} \text{ cm}$$

$$r_0^2 = (7.940\,30 \pm 0.000\,21) \cdot 10^{-26} \text{ cm}$$

Thomson cross section

$$(8/3)\pi r_0^2 = (6.652\,05 \pm 0.000\,18) \cdot 10^{-25} \text{ cm}^2$$

Fine structure doublet separation in hydrogen

$$\Delta E_H = (1/16)R_H \alpha^2 [1 + \alpha/\pi + (5/8 - 5.946/\pi^2)\alpha^2] =$$

$$= (0.365\,871 \pm 0.000\,003) \text{ cm}^{-1}$$

$$= (10\,968.56 \pm 0.10) \text{ Hz}^{-1}$$

Fine structure separation in deuterium

$$\Delta E_D = \Delta E_H R_D/R_H = (0.365\,970 \pm 0.000\,003) \text{ cm}^{-1}$$

$$= (10\,971.54 \pm 0.10) \text{ Hz}^{-1}$$

Zeeman displacement per gauss

$$e/4\pi mc^2 = (4.668\,85 \pm 0.000\,06) \cdot 10^{-5} \text{ cm}^{-1} \text{ G}^{-1}$$

Boltzmann's constant

$$k = R_0/N = (1.380\,44 \pm 0.000\,07) \cdot 10^{-16} \text{ erg deg}^{-1}$$

$$= (8.616\,7 \pm 0.000\,4) \cdot 10^{-5} \text{ eV deg}^{-1}$$

$$1/k = (11\,605.4 \pm 0.5) \text{ deg eV}^{-1}$$

First radiation constant

$$c_1 = 8\pi hc = (4.991\,8 \pm 0.000\,2) \cdot 10^{-15} \text{ erg cm}$$

Second radiation constant

$$c_2 = hc/k = (1.438\,80 \pm 0.000\,07) \text{ cm deg}$$

Atomic specific heat constant

$$c_2/c = \hbar/k = (4.799\,31 \pm 0.000\,23) \cdot 10^{-11} \text{ s deg}$$

Wien displacement law constant (*)

$$\lambda_{\text{max}} T = c_2/4.965\,114\,23 = (0.289\,782 \pm 0.000\,013) \text{ cm deg}$$

Stefan-Boltzmann constant

$$\sigma = (\pi^2/60)(k^4/\hbar^3 c^2) = (0.566\,87 \pm 0.000\,10) \cdot 10^{-4} \text{ erg cm}^{-2} \text{ deg}^{-4} \text{ s}^{-1}$$

(*) The numerical constant 4.96511423 is the root of the transcendental equation $x = 5(1 - \exp[-x])$.

TABLE VI: *continued.*

Sackur-Tetrode constant

$$\begin{aligned}
 S_0/R_0 &= \frac{5}{2} + \ln [(2\pi R_0)^{\frac{1}{2}} h^{-3} N^{-4}] = \\
 &= -5.57324 \pm 0.00007 \\
 S_0 &= -(46.3524 \pm 0.0020) \cdot 10^7 \text{ erg mole}^{-1} \text{ deg}^{-1} \\
 &\quad \text{(physical scale)}
 \end{aligned}$$

Sackur-Tetrode constant

$$\begin{aligned}
 S_0/R_{0\text{Ch}} &= -5.57256 \pm 0.00007 \\
 S_0 &= -(46.3467 \pm 0.0020) \cdot 10^7 \text{ erg mole}^{-1} \text{ deg}^{-1} \\
 &\quad \text{(chemical scale)}
 \end{aligned}$$

Bohr magneton

$$\begin{aligned}
 \mu_0 &= \hbar e / 4\pi m c = \frac{1}{2} \epsilon \hbar^2 c_{\text{e.s.}} \\
 &= (0.92731 \pm 0.00002) \cdot 10^{-20} \text{ erg G}^{-1}
 \end{aligned}$$

Anomalous electron moment correction

$$\begin{aligned}
 1 + \alpha/2\pi - 2.973\alpha^2/\pi^2 = \mu_e/\mu_0 &= 1.001145358 \pm 0.000000005 \\
 &\quad \text{(computed using adjusted value} \quad 1/\alpha = 137.0373 \pm 0.6000)
 \end{aligned}$$

Magnetic moment of the electron

$$\mu_e = (0.92837 \pm 0.00002) \cdot 10^{-20} \text{ erg G}^{-1}$$

Nuclear magneton

$$\begin{aligned}
 \mu_n &= \hbar e / (4\pi m_p c) = \mu_0 N m / H^+ = \\
 &= (0.505038 \pm 0.000018) \cdot 10^{-23} \text{ erg G}^{-1}
 \end{aligned}$$

Proton moment

$$\begin{aligned}
 \mu_p &= (2.79275 \pm 0.00003) \text{ nuclear magnetons} \\
 &= (1.41044 \pm 0.00004) \cdot 10^{-23} \text{ erg G}^{-1}
 \end{aligned}$$

Gyromagnetic ratio of the proton in hydrogen (uncorrected for diamagnetism)

$$\gamma' = (2.67523 \pm 0.00004) \cdot 10^4 \text{ rad s}^{-1} \text{ G}^{-1}$$

Gyromagnetic ratio of the proton (corrected)

$$\gamma = (2.67530 \pm 0.00004) \cdot 10^4 \text{ rad s}^{-1} \text{ G}^{-1}$$

Multiplier of (Curie constant) $^{\frac{1}{2}} x^{\frac{1}{2}}$, to give magnetic moment per molecule

$$(3k/N(x)^{\frac{1}{2}} = 2.6178 \pm 0.00010) \cdot 10^{-20} \text{ (erg mole deg}^{-1})^{\frac{1}{2}}$$

Mass-energy conversion factors

$$\begin{aligned}
 1 \text{ g} &= (5.61000 \pm 0.00011) \cdot 10^{26} \text{ MeV} \\
 1 \text{ electron mass} &= (0.510976 \pm 0.000007) \text{ MeV} \\
 1 \text{ atomic mass unit} &= (931.141 \pm 0.010) \text{ MeV} \\
 1 \text{ proton mass} &= (938.211 \pm 0.010) \text{ MeV} \\
 1 \text{ neutron mass} &= (939.505 \pm 0.010) \text{ MeV}
 \end{aligned}$$

Quantum energy, E , conversion factors

$$\begin{aligned}
 1 \text{ eV} &= (1.60206 \pm 0.00003) \cdot 10^{-12} \text{ erg} \\
 E/\tilde{\nu} = \hbar c &= (1.98618 \pm 0.00007) \cdot 10^{-16} \text{ erg cm} \\
 E\lambda_g &= (12397.67 \pm 0.22) \cdot 10^{-8} \text{ eV cm} \\
 E\lambda_s &= (12372.44 \pm 0.16) \text{ kV } \mathcal{X}\text{-units} \\
 E/\nu &= (6.62517 \pm 0.00023) \cdot 10^{-27} \text{ erg s} \\
 &= (4.13541 \pm 0.00007) \cdot 10^{-15} \text{ eV s}
 \end{aligned}$$

TABLE VI: *continued.*

$$\begin{aligned}\tilde{\nu}/E &= (5.03479 \pm 0.00017) \cdot 10^{15} \text{ cm}^{-1} \text{ erg}^{-1} \\ &\quad - (8066.03 \pm 0.14) \text{ cm}^{-1} \text{ eV}^{-1} \\ \nu/E &= (1.50940 \pm 0.00005) \cdot 10^{26} \text{ s}^{-1} \text{ erg}^{-1} \\ &= (2.41814 \pm 0.00004) \cdot 10^{14} \text{ s}^{-1} \text{ eV}^{-1}\end{aligned}$$

de Broglie wavelengths $\lambda_{B..}$, of elementary particles (*)

Electrons

$$\begin{aligned}\lambda_{B..e} &= (7.27377 \pm 0.00006) \text{ cm}^2 \text{ s}^{-1}/V \\ &= (1.552257 \pm 0.000016) \cdot 10^{-13} \text{ cm (erg)}^{\frac{1}{2}}/(E)^{\frac{1}{2}} \\ &= (1.226378 \pm 0.000010) \cdot 10^{-7} \text{ cm (eV)}^{\frac{1}{2}}/(E)^{\frac{1}{2}}\end{aligned}$$

Protons

$$\begin{aligned}\lambda_{B..p} &= (3.96149 \pm 0.00005) \cdot 10^{-3} \text{ cm}^2 \text{ s}^{-1}/V \\ &= (3.62253 \pm 0.00008) \cdot 10^{-15} \text{ cm (erg)}^{\frac{1}{2}}/(E)^{\frac{1}{2}} \\ &= (2.86202 \pm 0.00004) \cdot 10^{-9} \text{ cm (eV)}^{\frac{1}{2}}/(E)^{\frac{1}{2}}\end{aligned}$$

Neutrons

$$\begin{aligned}\lambda_{B..n} &= (3.95603 \pm 0.00005) \cdot 10^{-3} \text{ cm}^2 \text{ s}^{-1}/V \\ &= (3.60204 \pm 0.00008) \cdot 10^{-15} \text{ cm (erg)}^{\frac{1}{2}}/(E)^{\frac{1}{2}} \\ &= (2.86005 \pm 0.00004) \cdot 10^{-9} \text{ cm (eV)}^{\frac{1}{2}}/(E)^{\frac{1}{2}}\end{aligned}$$

Energy of 2200 m/s neutron

$$\begin{aligned}E_{2200} &= (0.0252973 \pm 0.0000003) \text{ eV} \\ T_{2200} &= (293.585 \pm 0.012) ^\circ\text{K} \\ &= (20.435 \pm 0.012) ^\circ\text{C}\end{aligned}$$

The Rydberg and related derived constants

$$\begin{aligned}R_\infty &= (109737.309 \pm 0.012) \text{ cm}^{-1} \\ R_\infty c &= (3.289848 \pm 0.000003) \cdot 10^{15} \text{ s}^{-1} \\ R_\infty hc &= (2.17958 \pm 0.00007) \cdot 10^{-11} \text{ erg} \\ Rhc^2 e^{-1} \cdot 10^{-8} &= (13.60488 \pm 0.00022) \text{ eV}\end{aligned}$$

Hydrogen ionization potential

$$\begin{aligned}I_0 &= R_H(hc^2/e)(1 + \frac{1}{4}\alpha^2 + \dots) \cdot 10^{-8} = \\ &= (13.59765 \pm 0.00022) \text{ eV}\end{aligned}$$

(*) These formulae apply only to nonrelativistic velocities. If the velocity of the particle is not negligible compared to the velocity of light, c , or the energy not negligible compared to the rest mass energy, we must use $\lambda_{B..D} = \lambda_c [\epsilon(s+2)]^{-\frac{1}{2}}$ where λ_c is the appropriate Compton wavelength of the particle in question and ϵ is the kinetic energy measured in units of the particle rest-mass.

REFERENCES

- [1] J. W. M. DuMOND and E. R. COHEN: *Rev. Mod. Phys.*, **25**, 691 (1953).
- [2] E. R. COHEN: *Phys. Rev.*, **88**, 353 (1952).
- [3] R. T. BIRGE: *Reports on Progress in Physics*, **8**, 90 (1941).

- [4] W. N. BOND: *Phil. Mag.*, **10**, 994 (1930); **12**, 632 (1931).
- [5] R. T. BIRGE: *Phys. Rev.*, **40**, 228 (1932).
- [6] R. A. BETH: *Phys. Rev.*, **53**, 681 (1938).
- [7] J. W. M. DUMOND: *Phys. Rev.*, **56**, 153 (1939).
- [8] C. F. GAUSS: *Theoria Combinationum Observationum Erroribus Minimis Obnoxiae, Werke*, Bd. **4** (Göttingen, 1873).
- [9] E. WHITTAKER and G. ROBINSON: *Calculus of Observations* (London, 1944), p. 218.
- [10] E. WHITTAKER and G. ROBINSON: *Calculus of Observations* (London, 1944), p. 224.
- [11] E. R. COHEN: *Rev. Mod. Phys.*, **25**, 705 (1953).
- [12] A. C. AITKEN: *Proc. Roy. Soc. Edinburgh*, **55**, 42 (1935).
- [13] E. R. COHEN: *Phys. Rev.*, **101**, 1641 (1956).
- [14] J. W. M. DUMOND: Preceding paper in this issue.
- [15] J. W. M. DUMOND and E. R. COHEN: *Rev. Mod. Phys.*, **25**, 691 (1953).
- [16] E. R. COHEN, J. W. M. DUMOND, T. W. LAYTON and J. S. ROLLETT: *Rev. Mod. Phys.*, **27**, 363 (1955).
- [17] D. R. TRIGGER: *Bull. Am. Phys. Soc.*, **1**, 220 (Abstract UAS) (1956).
- [18] D. J. COLLINGTON, A. N. DELLIS, J. H. SANDERS and K. C. TURBERFIELD: *Phys. Rev.*, **99**, 1622 (1955).
- [19] R. A. FISHER: *Statistical Methods for Research Workers* (Edinburgh, 1952), Table XIV.

Survey of Atomic Constants.

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[Di questa Relazione generale, già pubblicata per disteso in un fascicolo a parte del *Supplemento al Nuovo Cimento* (precisamente nel n. 2, 1° Semestre 1957), gli Autori hanno voluto preparare per questi « Rendiconti » il riassunto che qui sotto riportiamo. (N.d.R.).]

Résumé. — The authors have collaborated in a survey of the atomic constants, which was completed in August, 1955. Any such project begins, of course, with an attempt to survey all data which may be useful in determining the best values of the constants. From this mass of data one then selects the items of greatest accuracy, which are usually sufficient to overdetermine the desired constants. The best values are next calculated by an appropriate statistical method, such as the method of least squares. Thus there results a single, consistent set of values, with estimated errors, which can be recommended for general use until the available experimental data change significantly.

The first really comprehensive review in the field was carried out by R. T. BIRGE in 1929; he remained the leading authority for almost twenty years thereafter. In the postwar period two groups have been active in America—DuMOND and COHEN and their co-workers on one hand and BEARDEN and co-workers on the other. In Germany, STILLE has carried on the same type of investigation.

The present report is an outgrowth of the BEARDEN, EARLE, MINKOWSKI, and THOMSEN evaluation in 1953. This study pointed up certain discrepancies in λ_g/λ_s , the conversion factor from Siegbahn X-units to the absolute scale. A new investigation was undertaken in an attempt to resolve this dilemma; it developed into a rather comprehensive survey, including some data which is chiefly of historical interest.

As we have said, this survey was completed in August 1955. A few of the principal conclusions will now be noted. At the end of this paper more recent work will be discussed.

1) As in other recent evaluations, the errors of the various atomic constants were found to be of the order of 10 parts per million.

2) It was considered necessary to omit all X-ray « h/e experiments », that is measurements of the high frequency limit of the continuous X-ray spectrum. While

the experimental accuracy of the direct measurements would still warrant their inclusion, it now appears that their theoretical interpretation involves so much uncertainty that the final results carry no appreciable weight.

In such experiments, the usual procedure has been to set the X-ray spectrometer



Fig. 1.

for a constant wave-length, vary the voltage applied to the X-ray tube, and observe the intensity as a function of voltage. The resulting curve is called an isochromat. A typical experimental curve for tungsten is shown in figure 1. The ideal isochromat has, of course, been blurred by the limited resolving power of the spectrometer, energy spread of the electrons incident on the target, and other causes. DUMOND and BOLLMAN considered this problem about twenty years ago. They first assumed that the ideal isochromat consisted of a series of straight lines and intersected

the axis with a finite slope as shown by the solid curve in figure 2. Under this assumption they showed that the proper procedure for locating the cut-off point on the experimental curve is to choose the point where the second derivative is a maximum. However, they also considered the possibility that there might be a discontinuity in the ideal isochromat at the cut-off voltage as shown by the dotted curve; under this circumstance they showed that the maximum first derivative of the experimental curve gives the true cut-off.

Sommerfeld's theoretical analysis, as well as a limited amount of experimental evidence, indicated that the ideal isochromat for a very thin target had a discontinuity at cut-off and was constant above this point. This is shown in figure 3a. A thick target could be considered as a superposition of many thin layers, as shown in figure 3b. If the incident electrons lost energy more or less continuously in penetrating the target, each layer would contribute a thin target isochromat displaced from the preceding one by the average energy loss.

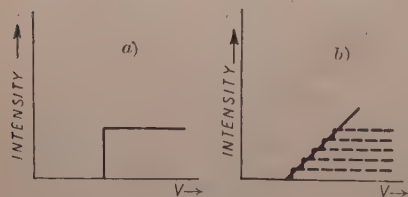


Fig. 3.

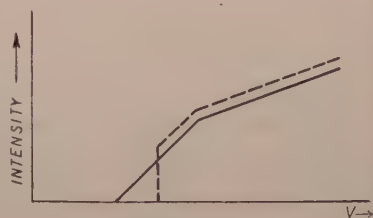


Fig. 2.

When the layers considered are made infinitesimally thin, the solid line results. Hence the use of the maximum-second-derivative criterion of DUMOND and BOLLMAN was indicated. This practice was long followed without much further question.

However, there is now much evidence, for example, the work of MARTON and LEDER, that electrons do not lose energy continuously in penetrating a thick target. Indeed it appears

that many penetrate to considerable depths with no appreciable energy loss whatever. This would indicate a probable discontinuity in the ideal curve as cut-off. Hence it would seem that the maximum-first-derivative criterion should be used. The situation is further complicated by the existence of fine structure in the tungsten isochromat near cut-off, which would modify somewhat the conclusions of DUMOND and BOLLMAN.

In addition to these factors, there is strong external evidence against the « h/e experiments », as shown in figure 4. This shows the value of λ_g/λ_s , the conversion factor from Siegbahn X-units to absolute units. The ruled grating measurements are basically direct determinations not involving the use of additional physical constants.

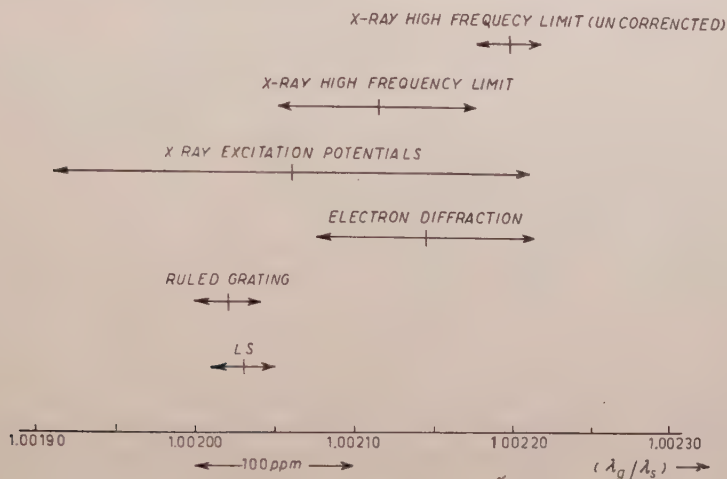


Fig. 4.

For other experiments, the values of various atomic constants are first calculated *without* use of X-ray data; these values plus an X-ray experiment will then yield a value of λ_g/λ_s . It is clear that the ruled grating determinations and the various crystal experiments are in fair agreement, while the value obtained from the X-ray « h/e experiments » are in marked disagreement with both.

Thus both internal and external evidence indicate that these experiments should not be used in evaluation of constants at this time. A better theory of the ideal isochromat might bring them back into the picture once more.

3) While the discrepancy involved in the « h/e experiments » has been tentatively explained, the situation with regard to the faraday has become much less satisfactory. For many years there were two accurate values of the faraday available, based on silver and iodine; both dated back to the 1914-16 era. While these have been revised from time to time as better values of the atomic weights became available, there has remained a serious discrepancy between the two figures. A few years ago two electromagnetic experiments—the cyclotron frequency of the proton and the gyromagnetic ratio of the proton—gave a very accurate indirect determination of the faraday. This electromagnetic faraday was in almost perfect agreement with the iodine value, but substantially higher than the silver one. This situation may be seen by comparing the electromagnetic, old I, and Ag values. Such a comparison suggested the possibility of some unknown systematic error in the work on silver; hence we considered dropping this value entirely.

However, the situation was drastically changed by two recent developments. When the iodine result is corrected for the most recent mass spectroscopic atomic weight, it is lowered to a value intermediate between the silver value and the electromagnetic one. Furthermore CRAIG and HOFFMAN have made a new determination with sodium oxalate

and have reported a result even lower than that for silver. Thus there are now three electrochemical values in fair agreement with one another and all significantly lower than the electromagnetic figure, which is substantially equal to recent adjusted values of the faraday. Hence there now seems little justification for omitting the silver value. Therefore a weighted mean of all chemical data was used, with error based on external consistency; it played a significant part in the final evaluation.

4) At the time of the survey, the authors concluded that there was still some experimental evidence for a variation of the velocity of light with frequency. With a single exception, all modern microwave results are in reasonable agreement with the presently accepted value for c . BERGSTRAND's optical measurements also confirm this figure. However, the mean of the older and less precise optical values is significantly lower, the difference being about 17 km/s. After a careful study of these older experiments as well as various critical reviews of them, the authors were not satisfied that the discrepancy had been explained. Hence the experimental verification of the constancy of the velocity of light seemed to rest primarily on BERGSTRAND's work: it appeared that a systematic error in this experiment might reopen the entire question.

However, BERGSTRAND's work appeared to be very careful and painstaking; no probable source could be found for an error of the order of 17 km/s. Furthermore, there were two recent determinations of c based on measurements of molecular band constants by both optical (infra-red) and microwave techniques; these both confirm the presently accepted value. While these cannot be regarded as pure optical determinations, it is our opinion that they are primarily such. Finally, there were a number of indirect considerations which seemed to preclude any variation in c . Thus the weight of evidence seemed to be against any such variation.

A few recent developments will now be briefly noted:

1) The last point, regarding the velocity of light, has resulted in more correspondence and discussion than any others. As a result, the authors have learned of three additional measurements using Bergstrand's geodimeter, in Sweden, Great Britain and Australia. The results were only about two parts per million lower than BERGSTRAND's value. In at least one of these runs the frequency of the crystal was recalibrated independently. Since all of these optical determinations use the same apparatus as that of BERGSTRAND, they are not completely independent. However, they have used many base lines of various lengths and it is difficult to imagine a significant systematic error which is completely independent of the length of the base line. The authors still feel that confirmation of this result by an entirely independent optical experiment, preferably in vacuum, would be highly desirable. However, the need for such confirmation is certainly not as great as it formerly appeared to be.

2) Almost simultaneously with the completion of our report, DUMOND, COHEN, and co-workers published a new adjustment of the atomic constants. This was essentially a systematic review of their data used in 1952, with the elimination of certain items believed to involve serious systematic errors. It was reassuring to find that their conclusions as to systematic errors in the « h/e experiments » were essentially the same as ours. However, due to the particular method of selecting data which they adopted, they retained the least accurate of three « h/e experiments » in their final adjustment. We feel that the logical course is to reject all three although the practical effect of this difference is small.

We also differ in use of the electrochemical data. DUMOND and COHEN considered the older value for the iodine faraday and the silver value; the errors assigned to both appear very low. They concluded that the silver value should be rejected just as we

once tentatively did during the early stages of our work. However, with the revision of the iodine data and the inclusion of the CRAIG and HOFFMAN work, we believe that there is no longer a good basis for rejecting the silver result. As a result, our values of the faraday and Avogadro's number are appreciably lower.

Finally DUMOND and COHEN used Birge's average for the measurement of Avogadro's number by crystal density and lattice constants determined from X-rays. In our case this value was lowered appreciably as a result of new data on calcite. However, a still more recent series of precision measurements by SMAKULA and co-workers indicates that the Birge average should be raised. Thus the DUMOND and COHEN position in this respect may now be a safe middle ground. At any rate, the effect of this difference on the final values of the constants is small, except in the case of λ_g/λ_s .

3) The electromagnetic value of the faraday should soon be known with much greater accuracy. The cyclotron frequency of the proton has now been determined by two different methods in three experiments (SOMMER, THOMAS and HIPPLE; SANDERS and co-workers, and TRIGGER); after a recent refinement of the TRIGGER calculations all are in reasonable agreement. The gyromagnetic ratio of the proton has been measured in a new experiment with an iron-free field by KIRCHNER and WILHELMY, who have reported a much higher value than THOMAS, DRISCOLL, and HIPPLE; however they plan to continue their study. Meanwhile work is well underway at the Bureau of Standards on a new and more accurate measurement, using an iron-free field. We understand that the Bureau also eventually plans to make a new electrochemical measurement of the faraday with silver.

4) If these new experiments are successfully carried out and are in reasonable agreement, the principal uncertainty remaining will lie in the fine-structure constant α , as determined from the fine-structure of the $n = 2$ state of H. This measurement was carried out by TRIEBWASSER, DAYHOFF, and LAMB and is, we believe, a very careful and accurate determination. However, there is no datum of comparable accuracy in our evaluation to confirm this data. Such a confirmation could be obtained in two ways: *a*) by new microwave fine-structure measurements, either on the same line or a different one or *b*) by a more accurate theoretical interpretation of the hyperfine structure of H. The latter would require a theory of the distributed nature of the proton magnetic moment sufficiently accurate so that any uncalculated higher terms in the hyperfine structure equation would be of the order of 1 part per million or less. Whenever this can be done, extremely accurate experimental data are available to compute a second and highly precise value of α .

Present Status of Research on the Physical Constants at the (United States) National Bureau of Standards.

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Definition of the primary standards of measurement in terms of physical constants has been the hope of many physicists for years. The proposal by JACQUES BABINET [1] (1829), CLERK MAXWELL [2] (1870) and others to adopt the wavelength of light as the primary standard of length was probably the first step in this direction. As early as 1887, MICHELSON and MORLEY [3] proposed a « method of making sodium light the actual and practical standard of length. » In 1892-93, MICHELSON and BENOÎT [4] accurately measured the wavelength of the cadmium red line in terms of the metre. MAXWELL (1870) also suggested taking the periodic vibration of light as a standard of time and the masses of molecules as the standard of mass.

Since that time, ways have been found for defining the primary standard of time in terms of molecular and atomic frequencies instead of the rotational frequency of the earth, which is known to be variable. Advances in atomic physics have led to the hope that both primary and secondary standards can be further expressed in terms of physical constants.

It is interesting, therefore, to examine the precision with which the primary standards can be measured, and the precision with which various physical constants may be measured in terms of them. This will reveal how ready we are to transfer our reliance on prototype standards, which, constant as they seem to be, may be subject to gradual change, to physical constants in the immutability of which we have great confidence.

1. - Measurement of primary standards.

Length. - The (United States) National Bureau of Standards maintains a group of 10 meter bars for determining standards of length. One of these,

« Meter 27 », is our national standard of length and has been compared with the standards of the International Bureau of Weight and Measures (BIPM) several times. These meter bars are regularly intercompared, so that the corrections of each with respect to the others are known. From $n(n-1)/2$ intercomparisons (45 for this group of bars) a probable error of 3 parts in 10^8 is attained [5]. By employing a partially balanced incomplete block experiment design, the same precision is obtained in 25 intercomparisons. Results of several comparisons of the U.S. national prototype meter with the BIPM meter indicate that the national meter is known to an accuracy within the above limit.

This precision is attained in comparing line standards which are approximately alike. Degradations in both precision and accuracy arise when lesser intervals of length are measured, the probable error in subintervals being roughly inversely proportional to the length of the interval. For the millimeter, for example, this is about 3 in 10^5 .

For lengths greater than 1 meter, the precision of measurement of the meter is almost achieved. Our 5-meter bar is measured in terms of one of our working standard meters with a probable error less than 2 in 10^7 , and 50-meter geodetic tapes are standardized in terms of the 5-meter bar with a probable error of 1 in 10^7 , (this is the precision obtained, not the accuracy «certified» by the Bureau.) Thus, geodetic tapes are known in terms of the BIPM meter with a probable error in accuracy (*) of between 2 and 3 in 10^7 . These are results of routine calibrations of first order geodetic tapes. If a requirement for greater accuracy existed, greater accuracy could be obtained.

End standards, or gage blocks, of the order of a few decimeters or less in length, are intercompared interferometrically with greater precision than line standards of the same length, but the calibration of end standards by reference to line standards, in particular to the BIPM meter, constitutes a problem. Work on this conversion is now in progress at the Bureau and is showing good agreement to within the limits of precision of the methods of measurement between end standards, measured directly in terms of wavelength of light, and line standards.

Wavelengths of light may be compared with a precision of about 1 in 10^9 [6], using suitable spectral lines *and the same interferometer*. If a slightly different experimental arrangement is employed, differences in the comparison results may be obtained which indicate uncertainties far greater than would be deduced from internal consistency of the data from a single experiment. Comparison of wavelengths measured by the National Physical Laboratory and the National Bureau of Standards show agreement to 1 in $5 \cdot 10^7$ or better [6]. There is reason to believe that the probable error in the accuracy of this comparison lies between 1 in 10^8 and 1 in 10^9 .

(*) See next page for explanation of this term.

When one attempts to measure material standards in terms of wavelength of light, much lower precision is obtained than when comparing wavelengths of different spectral lines. An individual end standard may be measured in terms of wavelengths with a precision of 1 in 10^8 , but when several similar end standards are measured and then intercompared, it becomes clear that the measurements are not as precise as internal consistency of the individual measurements indicated. Furthermore, if a set of end standards is measured interferometrically in several of the world's standardizing laboratories, the disagreement of the results obtained indicates a probable error of 1 in 10^7 for an individual laboratory [7]. This indicates the probable error in *accuracy* of measuring a gage block of the best quality in terms of wavelength of light, even though the number of wavelengths in a meter is regarded as precisely known. In further support of this view, we may consider the various determinations of the wavelength of the red line of cadmium in terms of the meter since 1892 (Table I).

TABLE I. — *Values of the wavelength of the cadmium red line in terms of the international meter (unit = $1 \cdot 10^{-10}$ m).*

Observers	Original values	Corrected and adjusted values in normal air	Differences 10^{-10} m	From mean parts per 10^6
MB	6 438.472 2	6 438.469 1	— 0.000 5	— 0.08
BFP	6 438.469 6	6 438.470 3	+ 0.000 7	+ 0.11
WI	6 438.468 5	6 438.468 2	— 0.001 4	— 0.22
SB	6 438.471 1	6 438.471 3	+ 0.001 7	+ 0.26
KL	6 438.467 2	6 438.468 9	— 0.000 7	— 0.11
SB	6 438.470 9	6 438.470 9	+ 0.001 3	+ 0.20
KL	6 438.468 5	6 438.469 0	— 0.000 6	— 0.09
KL	6 438.470 0	6 438.470 0	+ 0.000 4	+ 0.06
RVKB	6 438.467 7	6 438.468 7	— 0.000 9	— 0.14
	Means	6 438.469 6	\pm 0.000 9	\pm 0.14

MB: MICHELSON and BENOÎT, BIPM, 1892-93; BFP: BENOÎT, FABRY and PEROT, BIPM, 1905-06; WI: WATANABE and IMAIZUMI, Tokyo, 1927; SB: SEARS and BARRELL, NPL, 1933 and 1934-35; KL: KOSTERS and LAMPE, PTR, 1933, 1934-35 and 1937; RVKB: ROMANOVA, VARLICH, KARTASHEV and BARTARCHUKOVA, Leningrad, 1940.

Neither the individual determinations nor their deviations from the mean show any trend with time, thus exhibiting consistency of the procedures with the years and demonstrating the stability of the platinum-iridium meter bars within the precision of the observations. The probable error of a single determination based on deviations from the overall mean is 12 in 10^8 , giving a probable error for the mean of all of 4 in 10^8 . Thus, the wavelength

of light is known in terms of the meter to approximately the same accuracy that our national standard meter bar is known with respect to the BIPM meter.

Mass. — Similarly, a group of kilograms is maintained for determining standards of mass, one of which, « Kilogram 20 », is our national standard and has been compared with the BIPM unit a number of times. In comparing two similar kilograms in our laboratory, a probable error of 5 in 10^9 is ordinarily attained from two sets of reverse weighings which can be performed in two days.

At this point, it may be well to digress and discuss the limits of precision for all standards mentioned in this paper. The limits stated are those which are achieved with a reasonable effort. Greater precisions could be achieved in all cases by more extended observation. Since the precision increases as the square root of the number of observations, an inordinate effort must be put forth to appreciably increase the precision. In view of systematic errors which may enter into intercomparisons, further improvement of the precision is of doubtful value. For example, the correction to the standard kilogram for water sorption is about 1 in 10^9 for a 2% change in relative humidity, and the coefficient for this correction is not exactly known, while the meter bar is subject to thermal expansion amounting to about 9 in 10^8 for 0.01°C .

Degradation in both precision and accuracy develop when masses less than a kilogram are determined. The probable error for the accuracy of the gram is assessed to be about 14 in 10^8 , although without excessive effort a probable error of 7 in 10^8 could probably be obtained. Masses of the order of 1 gram can be compared with greater precision than the accuracy with which the gram is known. Masses greater than 1 kilogram can be assembled with the accuracy of the kilogram standard but with greater precision than that of the standard, although such masses cannot be compared with corresponding precision because suitable balances for the purpose are not available.

While we speak of comparing masses, it is important to remember that what we actually compare is the force exerted on those masses by the earth's gravitational attraction. If we try to measure masses in other ways, or to compare two forces, one of which is not gravitational, further complications are involved.

Time. — Responsibility for determination of time in the United States is assumed by the U.S. Naval Observatory. The National Bureau of Standards maintains the standard of frequency which is continuously checked with astronomical time, and broadcast in the standard frequency bands by radio stations WWV near Washington and WWVH in Hawaii with guaranteed accuracy of 1 in 10^8 . Corrections to the broadcast frequencies are later published making them accurate with a probable error of 1 in 10^9 .

The second of time is unique among standards. Until recently it was de-

finer as a certain part ($1/86400$) of a mean solar day. Since the average rotational speed of the earth may vary by almost 1 in 10^7 , the second of mean solar time did not represent an invariable standard [8]. Even within one year,

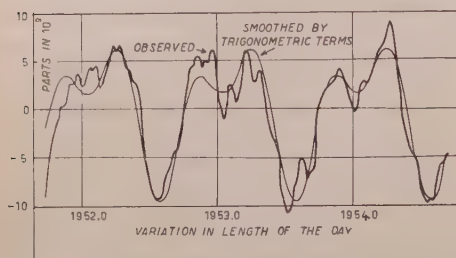


Fig. 1. — Variation in length of the day.

seasonal changes in the sidereal rotation of the earth amount to ± 1 in 10^8 . (See Fig. 1). Although this seasonal fluctuation has behaved rather regularly for the last few years, no great assurance is felt that it will continue to be regular in the future, or that irregular changes in the rotational speed, which have occurred in the past, will not occur again.

On the other hand, the orbital motion of the earth about the sun, and that of the moon about the earth, behave more regularly and furnish a basis for uniform time, called Ephemeris Time. For this reason the General Assembly of the International Astronomical Union adopted at Dublin in 1955 a definition of the second as a certain part ($1/31\,556\,925\,975$) of the tropical year 1900.0. This number precisely defines the second which is identical with the second of Ephemeris Time.

Using a group of carefully controlled crystal clocks for interpolation and nightly observation of the stars with a photographic zenith telescope, an accurate scale of relatively uniform time (UT2) may be established. This scale is based on the average sidereal rotational speed of the earth. During a year of observation, this scale was established by the Naval Observatory with an accuracy of about 1 in 10^9 in terms of the average speed of the earth during that year and checked against atomic frequency standards.

Relating the rotation of the earth to the relatively uniform scale of time is accomplished by assuming that the rates of the crystal clocks are monotonic functions of time and any periodic differences between star time and clock time are due to seasonal changes in the earth's rotational speed. Monotonic changes in the earth's rotational speed would not be detected by this means but would be interpreted as a change in rate of the clocks. It is this smoothed standard of time, called universal time (UT2), which is currently broadcast by the naval radio stations of the United States and the National Bureau of Standards stations WWV and WWVH.

To divide up this universal time scale into seconds as defined by the tropical year 1900.0, an extended series of observations on the moon is required. Data on the relative motions of the sun, moon, and earth compiled by astronomers for many centuries are also used. With data from additional moon observations from 20 cameras planned for the International Geophysical Year

1957-58 [9], it is hoped to determine the length of the second of Ephemeris Time in terms of our present universal time standard with a probable error in accuracy of about 1 in 10^9 . Thus, the second of time is defined more precisely than it is possible in the present state of the art to measure it.

During recent years, measurements have been made on the frequency associated with low-energy transitions of atoms and molecules in accordance with the relationship $E = h\nu$. One of the most useful of these for time measurements is the transition in the cesium atom involving the reversal of spin of a single electron which gives rise to the hyperfine structure of its optical spectra. The frequency associated with this transition has been measured by the National Bureau of Standards (9192.632 MHz) [10] and more recently with greater precision by the (British) National Physical Laboratory (9.192 631 83 MHz) [11]. At the present time, the precision with which the characteristic frequency of this atomic transition can be measured, appears to be better than the precision with which the average rotational speed of the earth can be measured over a one year period, and somewhat better than the accuracy with which the newly defined standard second can now be determined.

One important aspect of this atomic standard of time is that frequency can be measured by means of it as precisely in one second as can be done by astronomical means in more than one month.

Summary on primary standards. — We have shown that measurements may be made in terms of the three primary standards with precisions greater than 1 in 10^7 provided the thing to be measured is susceptible to measurement in the same way that the standards are measured and is within a certain range of magnitude. The quantity which is most accurately measured is time, and the least accurately, length. Time alone can be measured over a wide range of magnitudes (about 10^8 in normal practice) without appreciable impairment in accuracy. Both length and time may be measured in terms of physical constants and these constants may be determined in terms of the primary standards with about the same accuracy as similar primary standards may be measured. Intercomparisons may be conducted in terms of those physical constants more accurately than things can be directly measured in terms of the primary standards, and therefore one is led to consider the use of these constants as primary standards. So far, no ready means seems available for expressing the standard of mass in terms of a physical constant with suitable accuracy.

2. — Derived standards.

Relation to physical constants. — Of the physical constants, such as wavelength of light, the Rydberg constant, frequency of vibration for energy-level,

transitions and masses of molecules, atoms, and elementary particles, only a limited class, may be measured in terms of a single one of the primary standards. Many of elemental constants must be measured in terms of more than one of these primary standards. Since many of the physical constants involve electric or magnetic quantities, their measurement is accomplished best through derived standards of electric quantities.

Electric current. — The most useful of the derived standards in determining the physical constants is the ampere, because it is used as the link between the primary standards and electric and magnetic quantities in which many of the physical constants must be expressed.

The International Committee on Weights and Measures defined the « absolute » ampere as the current in two parallel straight conductors of infinite length and negligible cross-section which would produced $2 \cdot 10^{-7}$ MKS unit of force between them per meter of length in a vacuum when placed one meter apart. The definition thus permits the ampere to be determined in terms of the primary standards of mass, length, and time, without becoming involved in disputations about the dimensions for the permeability of space which is carefully cloaked in the definition.

Clearly, the definition does not set forth the best experimental procedure for measuring the absolute ampere. The usual experimental procedure is to coil the wires upon two forms and measure the force between the two forms when they are suspended coaxially from one arm of a balance and a current passes through the wires. When using such a current balance, measurements must be made on the diameters, pitch of the windings, and on the force between the coils. Since the wires on the forms are not measurable by the same techniques as line standards or gage blocks, a lower order of precision is obtained in measuring the diameters of the coils. Furthermore, the current flowing in the wire is not uniformly distributed throughout its cross-section so that even if the position of each turn of wire were exactly known, some uncertainty would still exist on the location of the current. Precision in « weighing » the current is decreased by the circumstance that in the arrangement used at the NBS, the additional weight required for balance when the current was reversed was about 1.5 grams, while the weight of the movable coil with its form was of the order of half a kilogram. Furthermore, since the dimensions of the coils and the size of the balancing weight are not close in magnitude to the primary standards (meter, kilogram) nor even sub-multiples of them, additional degradation in accuracy occurs with respect to what could be achieved in measuring optimum magnitudes.

Estimates of the experimental errors arising from various sources for a recent determination of the ampere by weighing, as assessed by the experimenters, are given in Table II. These errors are conservatively estimated

and probably represent a 90 percent confidence interval in most cases. These lead to an estimated error of 4 in 10^6 for a 90% confidence interval in the final result or a probable error of about 2 in 10^6 . These estimated errors do not include the error arising from uncertainty in the acceleration of gravity, g , which has been intentionally omitted in order to facilitate interlaboratory comparisons.

TABLE II. — Sources of error in determination of ampere and estimated magnitudes assigned by experimenters (CDC [12]) in ppm.

	Moving	Coil
	P_1 (*)	A_1 (*)
Adjustment of coil	1	1
Temperature of coil	1	1
Measurement of force	2	2
Lead corrections	2	2
Radius of fixed coil	1	1
Radius of moving coil	1	3
Finite cross section of moving coil	—	3
Distribution of current in wire	1	1
Calibration of standard mass	2	2
Root of sums of squares	4	6

(*) Designation of coil.

More recently, a new determination of the ampere has been made at the NBS using a Pellat balance [13]. In this case, measurement is made of the torque on a movable coil placed at right angles to a fixed coil. This experiment gave a value of the ampere smaller by 9 in 10^6 than that obtained 18 years earlier by the coaxial-coil balance, although the value of g was the same in both experiments. Investigations are under way to determine whether this difference is the result of the experimental procedure or is due to drifts in the standards of the volt and the ohm maintained by banks of standard cells and standard resistors at standardizing laboratories by means of which the ampere is realized [14]. However, the Pellat balance is probably not quite as accurate as the coaxial-coil balance. In this particular balance a correction of 6 in 10^6 had to be applied for the assumed distribution of current in the windings of the movable coil. At all events, the results from this entirely independent experiment may be regarded as a confirmation that there are no gross errors in the value of the ampere.

Altogether, there have been three highly precise determinations of the ampere using the coaxial-coil balance, one by the (British) National Physical Labor-

atory and two by the NBS [12]. These have been assigned weights by H. L. CURTIS [15] as shown in Table III. Estimating the probable error of the mean from the concordance of these values indicates that the ampere is known with a probable error of about 2 in 10^6 apart from the uncertainty in the transfer constant, g . This is not inconsistent with the conclusions reached from analysis of the accuracy of the individual experiment with the coaxial-coil balance previously described. We must, however separately examine the error introduced into the ampere by uncertainties in g .

TABLE III. - *Values of international ampere in terms of absolute ampere with weights assigned by H. L. CURTIS.*

Date	Experimenter	Value of international ampere	Weight
1934	CURTIS and CURTIS999 934	0
1935	DUPOUY and JOUAUST999 8	0
1936	VIGOUREUX999 863	3
1937	YONEDA and ISHIBASHI999 938	0
1939	CURTIS, CURTIS and CRITCHFIELD999 860	5
1939	VON STEINWEHR	1.000 04	0
1942	CURTIS, DRISCOLL and CRITCHFIELD . .	.999 856	5
	Weighted mean (Old value for gravity used)	.999 859	

Electric resistance and potential. - Although derived standards for electric resistance and potential are not as important in determining the physical constants, they will be briefly discussed because they serve to illustrate our problem. Having measured a current in absolute amperes with the balance and having related this current to an arbitrary voltage drop across an arbitrary resistor, that current may be reproduced in any laboratory by using calibrated replicas of those arbitrary standards of voltage and resistance.

The standards certified to other laboratories by the NBS are certified in terms of absolute volts and absolute ohms *as maintained at NBS*. For the above reason, the accuracy with which these derived standards is known does not affect the precision with which a standard ampere can be duplicated in those laboratories.

The absolute ohm is determined essentially by the comparison of an inductance with a resistance. In one type of experiment [16] the voltage drop in a resistor, produced by the rectified current induced in the secondary of a mutual inductor when a steady current in its primary is periodically interrupted, is compared with the voltage drop produced in a suitable resistor by

the same steady current. In another [17], the impedance of an inductor is compared with the impedance of a resistor for an alternating electromotive force. All of the methods require measurement of length (for determining the inductance) and time (for determining the frequency). Thus the ohm does not depend on knowing the transfer constant, g , since no measurement of force is required in determining it. The number of high precision determinations of the ohm is greater than for the ampere. These are listed in Table IV with the weights assigned by H. L. CURTIS. From them we can estimate the probable error of their weighted mean as 5 in 10^6 . This error is not inconsistent with the errors estimated by the experimenters.

TABLE IV. — *Values of international ohm in terms of the absolute ohm with weights assigned by H. L. CURTIS.*

Date	Experimenter	Value of international ohm	Weight
1936	CURTIS, MOON and SPARKS	1.000 454	2
1937	VIGOUREUX	1.000 499	1
1937	YONEDA	1.000 465	0
1937	HARTSHORN and ASTBURY	1.000 492 (*)	5
1938	JOUAUST, PICARD and HERON	1.000 520	2
1938	CURTIS, MOON and SPARKS	1.000 480 (°)	5
1939	ZICKNER	1.000 50	0
1939	WENNER, THOMAS, COOTER and KOTTER	1.000 487 (°)	3
	Weighted mean	1.000 487	

(*) Revised value, see G. H. Rayner: *Monograph* 95 I.E.E. 1955.

(°) Revised value, personal communication J. L. Thomas.

No precise direct determination of the volt in terms of the primary standards has been made. The absolute volt is a secondary type of derived standard determined by the ampere and the ohm. In fact, determination of the absolute ampere in practice is, in a sense, a determination of the absolute volt. Thus, the volt has an uncertainty which combines the uncertainty of both the ampere and the ohm. Neglecting the uncertainty in g , the probable error of the volt is slightly greater than 6 in 10^6 , in accordance with the above estimates.

Acceleration of gravity, g . — The acceleration, g , due to the earth's gravitational field, occupies a unique position in our system. Though often regarded as a physical constant, it is actually a geophysical quantity, variable from place to place, and at one place, variable from time to time. Its importance derives from the fact that usually when we precisely determine a derived standard

or a physical constant in terms of our primary standard of mass, we make use of g in our experiment as a transfer constant. When masses are being measured in terms of units of mass, lack of knowledge of the value of g is of no concern, since it acts alike on both the unknown mass and the standards of mass. However, when the force acting on a system not involving gravity is compared with the gravitational force acting on a mass, the accuracy of the value of g enters into the result.

Thus, uncertainty in g appears in the results of many determinations. That it affects the ampere and volt has already been pointed out. Even if the value of the ampere were determined by a method not involving g , the determination of the gyromagnetic ratio of the proton, as it was performed at the NBS would still be subject to the uncertainty in g , as well as the determination of the Faraday by physical methods. On the other hand, the accuracy of the Faraday, as determined by the electrochemical methods, would be independent of g , except insofar as g effects the ampere, because we can compare the mass of material deposited directly with the standards of mass.

Because of the ubiquity of g in physical measurements, it is of concern to look into the accuracy with which it is known and the precision with which the value of g in one laboratory can be related to that in another. The three most precise determinations of g that have been reported were performed by the pendulum method. A determination of g at Potsdam by KÜHNEN and FURTWÄNGLER [18] in 1906 resulted in a value higher by 17 in 10^6 than the value recommended by a gravity subcommittee of the (U.S.) National Research Council. In a re-examination of the Potsdam experiment, H. L. DRYDEN [19] concluded that too much weight had been placed on the observations on one of the several pendulums used which involved an extrapolation to zero mass, to allow for unknown corrections, and revised the Potsdam value by lowering it by 12 in 10^6 . This revised value, together with the other two results reduced

TABLE V. — *Value of acceleration of gravity reduced to Washington.*

Place	Date	Experimenters	Value (cm/s ²)
Potsdam	1906	KÜHNEN and FURTWÄNGLER: (old)	980.100
		(revised).	980.088
Washington	1936	HEYL and COOK	980.080
Teddington	1939	CLARK	980.084
Mean of last 3			980.084

to the Washington, D.C. base station is given in Table V. The probable error of the mean estimated from the concordance of those three values is 2 in 10^6 .

In assessing this error in the mean value of g , it must be remembered that great uncertainty attaches to estimates of probable error from a small sample. The theory of small samples tells us that there is a 5 percent chance that the true probable error derived from a set of three may be 4.4 times as great as the estimated one.

Furthermore, the three experiments which led to values in the table were performed with reversible pendulums and corrections were applied to the observations by the experimenters, not all of which could be directly observed, nor are thoroughly understood. Since these corrections, if incorrectly estimated or applied, are likely to affect all the experiments in the same way, the mean of the three values would be affected systematically. Thus, these estimates of the error in g are estimates of the precision of its determination with reversible pendulums, not estimates of the accuracy of g .

In performing the pendulum experiment, two quantities must be measured, length and time. The length required is the effective length, not while at rest but while swinging, which is calculated from the rest length and involves assumptions as to deformation of the knife edge, indentation of the support planes, motion of the supports, and bending and stretching of the pendulum. The possibility of error in these corrections is what lowers our confidence in the accuracy of g . The time measurement likewise is difficult, for the period of the pendulum changes in an irregular way while observations are being made, as a result of accumulating wear and damage to the knife edge.

Because of the importance of gravity in physical measurements, one is tempted to engage in the risky practice of assessing the systematic errors which may be present. There seem to be two main possible sources of error, correction for flexure of the pendulum and deformation of the planes and knife-edges. In HEYL's experiment [20], the flexure correction, determined theoretically, was different for different pendulums ranging from 2 to 7 in 10^6 . The results with different pendulums with the corrections applied were more concordant than without, but the precision of the measurements was not great enough that his outcome assures that the corrections were of the proper size, or even that they should not have been applied in the opposite sign. According to the theory developed by BESSEL, no correction need be applied for rolling on the knife edges if the knife edges are fixed and the planes are attached to the pendulum, as was the case in HEYL's experiment, and the radius of curvature of the knife edge is constant. If this theoretical condition is not fulfilled, or if the knife edge action is not a pure roll, one would estimate the possible error arising from this source to be no greater than an appreciable fraction of the ratio of the radius of curvature of the knife edge (about $10\ \mu\text{m}$) to the length of the pendulum. There is no evidence in HEYL's data to indicate different results with different sharpness of the knife edge, but again, the precision of the observations was not great enough to assure the absence of such

an effect. We may then assume that the systematic error from this source is certainly no greater than about 5 in 10^6 . Adding this error to possible flexure error, to be conservative, gives as the maximum systematic error in the value of g about 15 in 10^6 . It is interesting to note that this is just about the difference between HEYL's value and the value obtained by KÜHNEN and FURTWÄNGLER in extrapolating to zero mass.

Let us now consider the intercomparison of gravity measurements. As with other physical measurements, it is easier to compare two similar things with similar magnitudes than to measure either in terms of the primary standards. Thus, it is possible to compare gravity at two places with far greater precision than it can be accurately determined at one place. For places between which gravity differs appreciably, say about 1 gal, i.e. one centimeter per second per second, the difference may be measured with a probable error of 5 in 10^7 of the value of g , using conventional procedures. This is done by comparing the periods for a set of several precision pendulums each supported at the radius of gyration. The periods of such pendulums are relatively insensitive to changes in length. Since effectively the corrections that would be applied to the pendulums to obtain the absolute value of g are approximately the same at both places, errors in them enter the intercomparison as second or higher order. No doubt, with greater labor, even more precise comparisons of g can be achieved.

When the difference in g at two places is only 0.1 gal, the comparison can be effected with a probable error of 2 in 10^8 by using comparison gravimeters. A closed network including gravity stations at various latitudes in both Europe and North America, tied together by numerous pendulum and gravimeter intercomparisons, has a closing error of only 2 in 10^7 . Thus, an accurate determination of g at any station which can be tied into this network, would serve to establish the value for all stations in the network with degradation not exceeding 2 in 10^7 .

Having arrived at an estimate of the error in g , we may examine how this error affects the electric standards. The error in the absolute determination of the ampere resulting from an error in g is halved, because in the experiment the force on a mass in the gravitational field is balanced against the force of two identical currents acting on each other. Thus, the probable error in the ampere, allowing for the probable error in g , is increased slightly over the value previously given and lies between 2 and 3 in 10^6 . However, the previously mentioned caveats on the uncertainty in the estimate of this error must be remembered. The additional error due to the possible systematic error in g is not greater than 7.5 in 10^6 . It would appear, therefore, highly desirable to perform a determination of the ampere by a method which would eliminate the use of g as a transfer constant. The volt, which is derived from the ampere and ohm, is similarly affected.

The remarks made above about estimating the error in g apply to a much lesser extent to errors in the electric standards, although similar reservations must be placed on estimates of error from concordance of values in a small sample. Sources of error in the absolute determination of both the ampere and ohm are better understood and there is greater diversity in the experimental methods involved, particularly for the ohm. It may be assumed, then, that the electric standards are less likely to be affected by systematic errors than g , except to the extent that an error in g enters into the absolute value of the ampere and the volt.

Redetermination of gravity, g . — In determining values for some of the physical constants (velocity of light, wavelength of light, etc.), such concordance in results from highly independent experiments is obtained as to give great confidence in their accuracy. No such confidence can be held for the accuracy of g . For this reason, those physical constants, which directly or indirectly involve the primary standard of mass, are subject to uncertainty because of the use of g as a transfer constant in the experiments by which they are determined. Therefore, although g is not one of the physical constants, an accurate determination of it would remove one important source of uncertainty in the values of the constants which involve the primary standard of mass.

Two types of experiments are being planned at the Bureau to measure g , a pendulum method and a falling object method. In the present stage of our investigations, it appears that the greater accuracy may be obtained with a pendulum, but the free fall experiment is attractive because of its complete freedom from errors of the type that affect a pendulum.

We hope to achieve greater accuracy in the pendulum experiment by several devices. Instead of using reversible pendulums, we plan to use several pendulums each supported at four different effective lengths and to measure the differences in lengths and the differences in periods for each pendulum. The equations for the pendulum show that, by use of four positions, effects of rolling or sliding on the knife edges can be eliminated and this uncertainty in previous pendulum experiments can be removed. This procedure reduces somewhat the precision with which the observations can be made but improves the accuracy. Also we will design our pendulums so that the flexure correction for some will be almost negligible. By these procedures, we hope to remove the principal causes of doubt in the accuracy of g as heretofore determined with reversible pendulums.

We hope to improve considerably the precision of the observations themselves. As far as possible, lengths to be measured will be so selected that they can be compared readily with etalons which have been accurately measured. Timing of swing of the pendulums will be done by automatic optical-electronic techniques, so that *each swing* will be measured with a precision of 1 in 10^6 .

This has a number of advantages. It permits timing to be done more precisely on a smaller number of swings giving less wear on the knife edge so that it will be nearly the same for different positions of the pendulum. It will also afford an indication of changes in the knife edge between observations. With the method being planned, smaller amplitudes of vibration can be used so that correction to the period for amplitude of swing will be unimportant. In the HEYL experiment also the amplitude was so small that no correction was applied. In view of the accuracy with which end standards can be used to measure the differences in length of the pendulums, and the even greater accuracy with which the time of swing can be measured, it seems likely that an accuracy of a few parts in 10^7 can be achieved in the final result. At all events, the experiment is being so designed that sources of systematic error can probably be detected and evaluated.

Less optimism can be felt now for the accuracy obtainable in a free fall experiment. Various methods of timing and measuring distance have been considered, for the time and position must be measured with high precision at at least two points, preferably three, in the two dimensional time-length space. At one of these points, time will be changing rapidly with respect to length, at the other, length with respect to time. If an accuracy of 1 in 10^6 is desired, both of these must be measured with even greater accuracy, which is difficult. For example, after a free fall of one meter an object traverses one millionth of that distance in two ten millionths of a second. The situation involves a sort of uncertainty principle in that if one measures precisely where the object is he does not measure precisely when it was there, and conversely.

Among the methods which have been considered are (1) knocking a support away from an object and catching it on a lower anvil, (2) letting the object intercept a beam of light or electrons at several points along its path, and (3) dropping a corner reflector and measuring the time when white light fringes are formed by interference with light from several fixed mirrors at known separations. A number of experiments have been performed to test the feasibility of some of these methods, but the results do not indicate that either the accuracy or the precision of the pendulum experiment can be approached. However, we plan to perform a free fall experiment with the greatest precision we can attain, because of the importance of obtaining a value of g by other than a pendulum method.

Summary on derived standards. — We see that in proceeding from primary standards to physical constants certain derived secondary standards are often required, principal among which are the ampere and the transfer constant g . In determining these derived standards, the experimental procedures involved require measurements on a number of subsidiary quantities in each experiment,

such as the distances between wires in a coil. These, by their very nature, are not sharply defined and do not permit as precise a measurement as direct comparison of primary standards, nor do they always remain fixed during the experiment. Also, the subsidiary quantities are not close in magnitude to the primary standards in terms of which they are to be expressed. This adds to the difficulty and uncertainty in measuring them. As a result of these experimental errors, the precisions with which the secondary standards are known in terms of the primary standards are degraded by at least two orders of magnitude. Systematic errors which cannot be assessed accurately, particularly in the determination of g , increase the uncertainty in some of the measurements. One is inclined to wish that use of the earth's gravitation in determinations of physical constants could be limited to holding equipment on the laboratory tables, and that fundamental physics could be freed of being earthbound.

3. - Physical constants.

Physical constants and mensuration. - Because of the Bureau's close concern with problems of mensuration, interest in the physical constants has been active in our organization since its establishment. We have not established a broad comprehensive program of research on physical constants, but repeatedly in the course of our primary mission to establish and maintain national standards of measurement, the determination of certain physical constants is called for.

The precise determination of a physical constant rests upon precise mensuration. Brilliant experiments to determine the physical constants are often conceived and tried in university and other laboratories which sometimes lack the resources and the support of precise measuring techniques for their fullest exploitation. Such resources and techniques are usually found in the national standardizing laboratories of the various countries.

If, as we hope, certain physical constants will some day become our primary standards of measurement, it is the responsibility of these national standardizing laboratories to play their part in linking them to the present primary standards, and to come together in international meetings and agree on accepted values for international co-ordination. This places the National Bureau of Standards squarely in the business of determining physical constants in accordance with the responsibility with which we are charged.

Velocity of light, c . - The first determination of the velocity of light by the NBS was performed over 50 years ago [21]. It was made by comparing the computed capacity of a condenser in electrostatic units with its measured

capacity in electromagnetic units. The method is subject to errors of the type associated with the absolute determinations of the ohm. In those days, the absolute values of the electric standards were not well known. Applying corrections which we now know about to these old measurements, such as the present dielectric constant of air, leads to a value of $2.9980 \cdot 10^{10}$ cm per second, which differs only by 24 in 10^6 , from the value recommended by BEARDEN and THOMSEN [22]. However, this cannot be regarded as a highly precise determination. It is mentioned here only because of its historic interest and the additional confidence it gives us in the accuracy of the electric standards.

Two recent determinations of c have been performed by the Bureau employing entirely different methods. One of these was performed by radio frequency interferometry, and the other by infrared spectrometry using an interferometer for calibration.

In the radio experiment, [23], a base-line of 1500 meters was measured on the flat bed of a dry lake. Two receivers were set up at the ends of this base-line and two transmitters, operating on 173.8 MHz, were placed about 1400 meters from each receiver along the base-line extension. The phase of the signal arriving from each transmitter at both of the receivers was measured simultaneously by heterodyning them with the signal from a third transmitter operating on a slightly lower frequency. The phase difference of the signals arriving at the two receivers is given by

$$2\varphi = \varphi_1 - \varphi_2 + 4\pi n,$$

where φ_1 is the phase difference for the signals from one of the transmitters on the base-line, φ_2 for the other, and n is an integer readily determined. The phase velocity of propagation is given by

$$v = L\omega/\varphi,$$

where L is the path length and ω the angular frequency of the VHF transmitters. Applying corrections for the refractive index of the atmosphere gives c , the speed of light in vacuo.

The value obtained was $2.997951 \cdot 10^{10}$ cm s⁻¹ to which the experimenter assigned an error bound of 10 in 10^6 , comprising both constant and statistical errors. The major constant error arises from uncertainty in measurement of the base-line which is assigned a probable error less than 1 in 10^6 . Since the same base-line value was used in all the measurements, they would all be affected alike. Other systematic errors appear to be too small to influence the result in a major way. Because two base-line transmitters

were used (only one was necessary for a measurement), systematic differences in response of the two receivers and need for knowledge of auxiliary geometry were largely eliminated. Corrections were applied for other effects of the equipment, all of which are small.

Corrections for the refractive index of the atmosphere were computed from a formula obtained from the work of other investigators. Pressure, temperature, and water vapor content were measured at two points near the transmission path. The correction for refraction was about 250 in 10^6 and varied from day to day over an extreme range of 28 in 10^6 . Values of c obtained from measurements on single days exhibited an extreme range of 29 in 10^6 and were uncorrelated with the index correction. Properly taking into account the intra-daily and the inter-daily fluctuations, the probable error in the precision of the mean of the phase difference measurements was 2 in 10^6 . Thus, it would appear that the probable error of the value of c obtained from this experiment is slightly over 2 in 10^6 .

However, there are other sources of error, of small importance individually, but perhaps great in their aggregate, which are difficult to assess accurately. For example, a correction of 2 in 10^6 was applied to allow for effects of the ground which involves assumptions as to ground constants; reflections from mountains 8 to 30 km away produced an error which might be 2 in 10^6 ; errors produced by pick-up in the receiving antenna cables, undiscovered in the field tests, were subsequently found to have an effect which might be as great as 5 in 10^6 . For this reason, the probable error of the experimental result is larger than the naive estimate in the preceding paragraph and its value cannot be assessed with confidence.

The determination of c by infrared spectrometry [24] involves measurements of an entirely different type. The microwave spectral lines of carbon monoxide are given by

$$\nu = 2B_0(j+1) - 4D_0(j+1)^3$$

and the infrared lines are given by

$$\nu = \nu_0 + (B_1 + B_0)m + (B_1 - B_0 - D_1 + D_0)m^2 - 2(D_1 + D_0)m^3 - (D_1 - D_0)m^4,$$

where the capital letters are molecular constants, j the rotational quantum number and $m = j+1$ or $-j$, according to which branch of the spectrum is being considered. If the relationship in the first equation is measured in cycles per second, and that in the second equation in wave numbers per centimeter, then the quotient $B_0(1)/B_0(2) = c$ gives the velocity of light in cm per second. Fortunately, the frequency of the lines given by the first equation lies in a part of the microwave spectrum where their frequencies may be accurately measured. GILLIAM, JOHNSON, and GORDY [25] determined the frequency for

the first rotational line with an error stated as 2.5 in 10^6 . This approximately determines the constant B_0 since D_0 is smaller by $3 \cdot 10^6$. D_0 is a «stretching» constant, not unlike the stretching correction in the pendulum experiment. It can be calculated from B_0 , and has also been obtained experimentally by a measurement on the second rotational line by BEDARD, GALLAGHER, and JOHNSON [26], so that B_0 is determined from the microwave measurements nearly as precisely as ν itself.

Determination of B_0 in the second equation was performed by PLYLER, BLAINE, and CONNOR at the Bureau. Since the wavelengths of infrared lines could not be measured with the same precision as the frequency of the microwave lines, a large number of them were measured, 20 in the R branch and 23 in the P branch in absorption, and 15 in the P branch in emission. The constants of the second equation were calculated by least squares and the wavelengths recomputed from the constants. This affords a good means of determining the statistical probable error in $B_0(2)$ which turned out to be 13 in 10^6 . The error in $B_0(1)$ is trivial in comparison.

It is interesting to note that in this experiment the velocity of light is determined directly in terms of the red cadmium line as a primary standard of length. Since this line is known accurately in terms of the prototype meter, no significant error is introduced in expressing c in cm per second.

For comparison, the values obtained for c by some other methods are presented in Table VI together with the results of the experiments described above. The errors stated are probable errors which were assigned, in all cases except the first, by the experimenters.

TABLE VI. — *Values of c by various methods with errors assigned by experimenters.*

Experimenters	Method	Velocity (cm/s)	P.E. ppm
ROSA and DORSEY	Ratio of units	$2.9980 \cdot 10^{10}$	30
FLORMAN	Radio interferometry	2.997 951	3
PLYLER, BLAINE and CONNOR	Infrared spectrometry	2.997 92	13
ESSEN	Microwave cavity	2.997 925	3
FROOME	Microwave interferometry	2.997 930	0.6
ASLAKSON	Radio shoran	2.997 942	7
BERGSTRAND	Kerr cell	2.997 931	0.5

Because of the great importance of c as a physical constant, and because of the practical importance of c for geodetic surveying with the geodimeter developed by BERGSTRAND [27], the Bureau is planning a new determination of this constant. Two methods are being considered for the first attempts, although other methods may be employed also. One involves a refinement

of the PBC [24] experiment, and the other an optical determination using a Kerr cell as was used by BERGSTRAND, or some other electro-optical shutter.

It is thought that some refinements can be used in the PBC technique, permitting more precise measurements of the wavelengths. Also, greater automation may reduce the labor of measuring the lines so that more observations may be made. If adequate precision in the infrared measurements is obtained, redetermination of the microwave spectral frequency will be required.

In describing the PBC experiment, no consideration was given to systematic errors because it is thought that they are small compared with the statistical errors. If the precision of the experiment is greatly increased, the method must be scrutinized more closely to examine effects of them.

We hope to achieve the desired accuracy in the second experiment being planned, essentially a modern version of the Fizeau experiment, by a brute force technique. We plan to establish a base line about 5 km long with a high accuracy, approaching a probable error of 1 in 10^7 , by duplicating in the field, as far as it is possible, the same metrological techniques as are employed in our calibration of geodetic tapes. These tapes, as was pointed out before, are calibrated in terms of the prototype meter with a probable error in accuracy of about 20 in 10^8 . Even this figure, we believe can be improved somewhat by more careful measurement of our 5-meter bar. The work of BERGSTRAND and others has shown that, with a base line of the above length, measurements of the transit time of light pulses may be made with sufficient precision in a moderate number of observations such that the limit of error, which we hope to achieve for the base line, may be comparable with the error in the light measurements.

What we really hope to measure most precisely is u , the group velocity for wave packets of a defined spectral range in normal atmosphere. This is the quantity which must be accurately known for the geodetic application of the geodimeter. We plan to measure pressure, temperature, and humidity at a sufficient number of points along the path, so that reliable reduction to a vacuum may be made, using the spectroscopically determined constants for the reduction. Since the total correction to c for atmospheric refraction is only 3 in 10^4 , realization of our hopes in this experiment would make c better known than any of the other elemental physical constants at the present time.

It is interesting to consider the implications if the desired precision is achieved in both of these proposed experiments. In the first case, we have the value of c determined in terms of the standard of time, ultimately the ephemeris second, and the wavelength of the red line as a standard of length, in the other case, in terms of the same ephemeris second, and the prototype meter as a standard of length. As was pointed out before, we know the wavelength of red cadmium in terms of the prototype meter with an error of less than 1 in 10^7 for a 95% confidence interval. If the results of the two exper-

iments agree to within reasonable limits of assigned errors, we then have a closed chain of constants and a high degree of confidence in them. If they fail to agree so well, an error is indicated in either our experiments or our present day theoretical concepts.

Gyromagnetic ratio of the proton. — The gyromagnetic ratio of the proton γ_p plays a dual role in the family of physical constants. As a physical constant, known in the absolute sense with respect to the primary standards, it is a key link in the chain leading to our best values of N , e , h . (See for example BT [22]). Thus, this modern constant, unknown at the time of AVOGADRO, is appropriately a part of this centennial symposium in his honor. As a transfer constant, γ'_p it plays a role similar to that of g , allowing comparison of magnetic fields and of measurements involving them with a precision greater than the absolute value of either, (the prime indicates the value uncorrected for diamagnetism.) As a transfer constant it is only necessary to know the apparent value γ'_p in some standard fluid such as oil.

If H is an external magnetic field applied to a sample in which the nuclear precession angular frequency ω_n is to be measured

$$\omega_n = \gamma'_p H,$$

and

$$\gamma'_p = \frac{4\pi\mu'_p}{h},$$

where μ'_p is an apparent magnetic moment of the proton. In this discussion, the symbol H is used instead of B because this is a common practice. It is recognized that it is the flux density rather than the magnetizing field that is involved. If, however, proper diamagnetic corrections are made (27 ppm for H gas and ~ 2 ppm to water or oil BT [22], p. 69) so that H represents the field seen by the precessing protons

$$\omega_n = \gamma_p H \quad \text{and} \quad \gamma_p = \frac{4\pi\mu_p}{h}$$

When determined in this latter absolute sense γ_p gives information about μ_p and h . In either case, the determination of γ_p or γ'_p involves the absolute measurement of a frequency $\omega_n/2\pi$ and a magnetic field H .

The precise measurement of the frequency, with an accuracy far exceeding the need here, is no problem provided the frequency to be measured is well enough defined by the experimental arrangement. In the nuclear resonance absorption method used by THOMAS, DRISCOLL and HIPPLE [28], the error or

in specifying the resonance frequency to be measured is estimated at $4 \div 5$ in 10^6 , a small portion of the total error. The checking of this frequency against the primary standard was accomplished with an error of 1 in 10^6 , although it could readily have been done better.

The absolute determination of the magnetic field is the most difficult and painstaking portion of the measurement and contributes most to the experimental error. Included therein, in significant amount, are the uncertainties in the ampere and g . (See Table VII).

TABLE VII. — *Contributing errors in determining gyromagnetic ratio of proton estimated by experimenters.*

	Parts per million
Platinum-iridium mass	1
Precision of balance used in this experiment	9
Gravity	3
Experimental constant in measurement of the ampere in absolute units	10
Comparison of current with standards	3
Width of coil	10
Length standard	5
Field distribution	10
Neutralization of stray field at upper wires	5
Adjustment of resonance pip to reference point on oscilloscope	4
Calibration of Helmholtz coils used for field distribution	4
Resonance frequency	1
Effect of ferric ions in sample	4

The measurement was done with great care and is described in detail in the THOMAS, DRISCOLL and HIPPLE [28] paper. It represents a conscientious effort to determine the absolute value of a strong magnetic field with all the accuracy allowed by the current state of the art, and was done with full understanding that γ'_p as thus determined could become a reference standard for magnetic field determinations.

The values reported with more complete corrections applied are [29]

$$\gamma'_p = (2.675\,23 \pm 0.000\,06) \cdot 10^4 \text{ s}^{-1} \text{ G}^{-1},$$

$$\gamma_p = (2.675\,30_5 \pm 0.000\,06) \cdot 10^4 \text{ s}^{-1} \text{ G}^{-1}.$$

The estimated error is given as 22 in 10^6 which is thought to be several times the probable error and is based upon an array of individual errors shown in Table VII.

Since this determination of γ'_p only two others have been reported.

KIRCHNER and WILHELMY [30] (*) report the value

$$\gamma'_p = (2.67549 \pm .00016) \cdot 10^4 \text{ s}^{-1} \text{ G}^{-1},$$

based upon a determination at 100 G in a precision air core solenoid, using resonance absorption. Note this is γ'_p , uncorrected for diamagnetism.

The discrepancy (95 in 10^6) is about equal to the total combined errors of either (22+60). The authors [30] suggested that the reason for the difference lies in the conversion between the international and absolute amperes rather than experimental error.

LINDSTROM [31] has reported a value for γ'_p obtained by a different method. In essence, he is able to make the necessary determination of the absolute value of a magnetic field by measuring the radius of curvature, ρ of the path of $K+L$ internal conversion electrons from ThB whose energy difference is known from X-ray data. The value of γ'_p follows as before from a resonance measurement in the same field. LINDSTROM reports

$$\gamma'_p = (2.67525 \pm .0002) \cdot 10^4 \text{ s}^{-1} \text{ G}^{-1}.$$

Analysis of LINDSTROM's calculations shows that this is essentially a determination of ω_e/ω'_n not of γ'_p . The physical constants he used to arrive at H and thus γ'_p are based strongly on γ'_n as determined by THOMAS, DRISCOLL and HIPPLE, and ω_e/ω'_n as measured by GARDNER and PURCELL. When this dependence is removed, and the required value of $h/m_e c = \alpha^2/2R$ is computed from the independent constants α (fine structure) R (Rydberg) a new value of ω_e/ω'_n emerges, which is in surprisingly good agreement with the GARDNER and PURCELL value considering the uncertainties involved. λ_s/λ_g is also needed, but its accepted value is in agreement with the ruled grating determinations, i.e. γ_p is not again included.

This determination therefore does not lend support to the correctness of the THOMAS, DRISCOLL, HIPPLE value of γ'_p but does serve to emphasize the need for a new and, if possible, more accurate determination of γ'_p .

Because of the important way that γ'_p is linked to the determination of other physical constants, as shown by other speakers in this symposium, it is most desirable that the absolute value of γ'_p be determined by other national standardizing laboratories using similar and/or basically different methods of higher accuracy.

Accordingly, BRANSCOMB and BENDER at NBS are now engaged in a re-determination of γ'_p using a method of higher potential accuracy. The magnetic field will be established by the precision coil used for the recent determination of the ampere and be limited to about 12 gauss.

(*) Latest unpublished value forwarded to us by Dr. J. S. THOMSEN.

A free precession technique will be used with a spherical sample of pure water about 2 cm in diameter. The sample will first be placed in a strong field and then moved quickly to the standard weak field in the solenoid where the free precession frequency will be determined. To initiate the precession a « $\pi/2$ pulse» will be used to put the moment orthogonal to the weak field. It appears that the uncertainty of the result should be about the same as that of the absolute ampere.

Cyclotron resonance of the proton. — The determination of e/m_p , the ratio of electronic charge to mass of the proton, using cyclotron resonance methods by SOMMER, THOMAS and HIPPLE [33], followed closely upon the determination of γ_p . The measurement was made possible by their invention of a special vacuum tube, the omegatron. In it, protons produced on the axis by electron impact ionization of hydrogen are caused to spiral outward under the combined influence of an oscillating electric field between two parallel flat plates, and a steady uniform magnetic field parallel to the plane of the plates in which the omegatron is placed. A static axial electric trapping field is arranged to hold the spiralling protons within the region between the plates long enough to allow them to make the many revolutions required for the necessary resolution. When the oscillating electric field is related to the steady magnetic field according to the equation

$$\omega_c = \frac{eH}{m_p c},$$

the protons spiral outward far enough to reach a collector. At other frequencies the particles spiral outward to a maximum radius, then inward again as the phase relations change. Other masses behave similarly at appropriate values of ω so that the device becomes a simple mass spectrometer, allowing the comparison of masses by comparison of frequencies. Unfortunately, because of trapping difficulties, the omegatron has worked well only for light masses.

Fig. 2 shows the details of the omegatron. Its active volume is about 10 cm³.

As a consequence of the non-uniform axial trapping field, there exists also a radial component of electric field which causes a shift in the simple resonance condition. The correction to

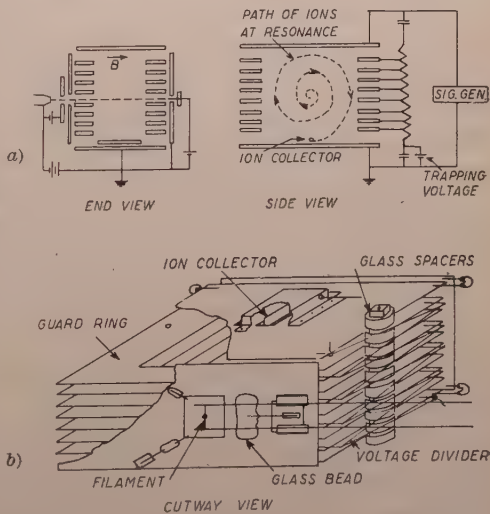


Fig. 2. — Simplified diagram of omegatron.

be applied can be computed relatively well, since the correction is small. However, there is an additional radial field due to space charge. This cannot be computed for lack of knowledge about the number of non-resonant ions trapped on the axis. Fortunately, the correction for both effects depends upon the mass of resonant ions, and it is possible to determine it experimentally by measurements at several masses (H^- , H_2^+ , D_2^+), taking advantage of the precise knowledge of mass ratios from known mass spectroscopic data.

Here again, as in the determination of γ_p , the basic requirements are a measurement of frequency and a magnetic field. It is convenient to use γ_p' as a transfer constant for the measurement of the field. Thus

$$H = \frac{\omega_n'}{\gamma_p'}$$

and

$$\omega_c = \frac{e}{m_p c} \frac{\omega_n'}{\gamma_p'}$$

or

$$\frac{e}{m_p c} = \gamma_p' \frac{\omega_c}{\omega_n'}$$

Of course, one can equally well use the values of γ_p corrected for diamagnetism and write

$$\frac{\omega_c}{\omega_n} = \frac{e}{m_p c \gamma_p} = \frac{e}{m_p c} \frac{\hbar}{4\pi\mu_p},$$

where we substitute for γ_p its value

$$\gamma_p = \frac{4\pi\mu_p}{\hbar}.$$

We see immediately that

$$\mu_p = \frac{\omega_n}{\omega_c} \cdot \frac{e\hbar}{4\pi m_p c} = \frac{\omega_n}{\omega_c} \cdot \mu_n,$$

i.e. the magnetic moment of the proton in nuclear magnetons.

The cyclotron resonance experiment in essence becomes an experiment to determine the value of the ratio

$$\frac{\omega_n'}{\omega_c} \quad \text{or} \quad \frac{\omega_n}{\omega_c},$$

i.e. the ratio of the two resonance frequencies in the same magnetic field.

The absolute value of the field is unimportant.

STH [33] report the value

$$\frac{\omega'_n}{\omega_e} = 2.792\,68_5 \pm .000\,06 \quad (23 \text{ ppm}).$$

The error is in the nature of a limiting error. From a study of their work, BEARDEN and THOMSEN [22] estimate a probable error of 7 in 10^6 . Applying the diamagnetic correction [29] of 28 ppm gives the corrected value

$$\frac{\omega_n}{\omega_e} = 2.792\,76 \pm .000\,06 \quad (23 \text{ ppm}),$$

or

$$\mu_p = (2.792\,76 \pm .0006) \text{ nuclear magnetons} \quad (23 \text{ ppm}).$$

BLOCH and JEFFRIES [34] have used an inverse cyclotron method to obtain $\omega_n/\omega_e = \mu_p/\mu_n$ and report $2.792\,45 \pm .000\,20$ nuclear magnetons (70 ppm). TRIGGER [35] repeated the measurement and reported experimental agreement but found that analysis of the equations of motion required a correction making the final result

$$\mu_p = (2.792\,75 \pm .00010) \text{ nuclear magnetons} \quad (35 \text{ ppm}).$$

Also using inverse cyclotron methods COLLINGTON, DELLIS, SANDERS, TURBERFIELD [36] obtained

$$\mu_p = (2.792\,81 \pm .00004) \text{ nuclear magnetons} \quad (15 \text{ ppm}).$$

No further work on the determination of ω_e/ω'_n , is contemplated at NBS at the present time.

It seems appropriate to deviate from the discussion of work at NBS to call attention to the analogous determination of the ratio ω_e/ω'_n for electrons performed by GARDNER and PURCELL [32]. This ratio along with γ'_p and ω_e/ω'_p forms a family of resonance constants of important significance in arriving at values of the elemental constants. In this case, the greater ω_e required an ingenious use of microwave techniques. They report the value

$$\frac{\omega_e}{\omega'_n} = 657.475 \pm .008. \quad (12 \text{ ppm}).$$

Fundamental constants derived with the aid of the resonance constants. — The resonance experiments give us the values for γ_p , γ'_p , ω_e/ω'_n , ω_e/ω'_p . It is interesting to combine them with the independent (*) precision constants, R_∞ , α ,

(*) BT [22] show that the correlation of α with the resonance constants is negligible. p. 99.

c , M_p , Rydberg constant, fine structure constant, velocity of light and atomic mass of the proton, respectively, and arrive at values of other important constants. The values of these constants are given in Table VIII.

TABLE VIII. - Values for the precision constants given by BEARDEN and THOMSEN with their errors.

$R_\infty = \frac{2\pi^2 m e^4}{c h^3} = (109\,737.31 \pm .01) \text{ cm}^{-1}$	0.1 ppm.
$c = (2.997\,928 \pm .000\,004) \cdot 10^{10} \text{ cm s}^{-1}$	1 ppm.
$\frac{1}{\alpha} = \frac{hc}{2\pi e^2} = 137.037\,1 \pm .000\,5$	3 ppm.
$M_p = (1.007\,595\,7 \pm .000\,001\,0) \text{ AMU (physical scale)}$	1 ppm.
$\gamma'_D = (2.675\,23 \pm .000\,06) \cdot 10^4 \text{ s}^{-1} \text{ G}^{-1}$	22 ppm.
$\gamma_D = (2.675\,30 \pm .000\,06) \cdot 10^4 \text{ s}^{-1} \text{ G}^{-1}$	22 ppm.
$\frac{\omega'_n}{\omega_c} = 2.792\,68 \pm .000\,06$	22 ppm.
$\frac{\omega_e}{\omega'_n} = 657.475 \pm .008$	12 ppm

The GARDNER and PURCELL value for $\omega_c/\omega'_n = \mu_0/\mu'_p$ is used here instead of the more precise combination of

$$\frac{\mu_s, \mu_0}{\mu'_D \mu_s} = \frac{658.229\,3}{1.001\,145\,4} = 657.476\,7 \pm .000\,6.$$

The values are essentially unaltered, and the results are then on an experimental basis alone. It is still desirable to verify the theoretical correction μ_0/μ_s by a more accurate determination of μ_0/μ'_D , where this becomes possible.

The list of derived constants in Table IX is not presented as a list of adjusted best values. This is best left to careful analyses like those of DUMOND and COHEN, or BEARDEN and THOMSEN. The list is presented primarily to show how the resonance constants can be used to arrive at precision values, and how their errors contribute to the uncertainty in the final value. This is presented more as a plea for the national standardizing laboratories to make a concerted effort to refine our knowledge of the resonance constants, for it is

TABLE IX. - *Values of derived constants and their errors.*

e	$= \frac{\alpha^3 c}{4\pi R \gamma'_p (\omega_e / \omega'_n)} = (4.8029 \pm .00013) \cdot 10^{-10} \text{ esu}$	
	$\sqrt{(9)^2 + (1)^2 + (22)^2 + 12^2} = \sqrt{710}$	$= 27 \text{ ppm.}$
m_e	$= \frac{\alpha^3}{4\pi R (\gamma'_p)^2 (\omega_e / \omega'_n)^2} = (9.1084 \pm .0004_6) \cdot 10^{-28} \text{ g}$	
	$\sqrt{(9)^2 + (44)^2 + (24)^2} = \sqrt{2593}$	$= 51 \text{ ppm.}$
h	$= \frac{\alpha^5 c}{8\pi R^2 (\gamma'_p)^2 (\omega_e / \omega'_n)^2} = (6.6252 \pm .0003) \cdot 10^{-27} \text{ erg s}$	
	$\sqrt{(15)^2 + (44)^2 + (24)^2} = \sqrt{2738}$	$= 52 \text{ ppm.}$
N	$= \frac{M_p 4\pi R (\gamma'_p)^2}{\alpha^3} \frac{\omega_e}{\omega'_n} \frac{\omega_c}{\omega'_n} = (6.0248 \pm .0003) \cdot 10^{23}$	
	$\sqrt{1 + (44)^2 + (12)^2 + (22)^2 + 9^2} = \sqrt{2646}$	$= 51 \text{ ppm.}$
F	$= M_p \gamma'_p \frac{\omega_c}{\omega'_n} = (9652.2 \pm 0.3) \text{ emu eq}^{-1}$	
	$\sqrt{1 + (22)^2 + (22)^2} = \sqrt{969}$	$= 31 \text{ ppm.}$
$\frac{m_p}{m_e}$	$= \frac{\omega'_n}{\omega_c} \frac{\omega_e}{\omega'_n} = 1836.12 \pm .04_6$	
	$\sqrt{(22)^2 + (12)^2} = \sqrt{628}$	$= 25 \text{ ppm.}$
$\frac{e}{m_e}$	$= e \gamma'_p \frac{\omega_e}{\omega'_n} = (5.27305 \pm 0.00013) \cdot 10^{17} \text{ esu/g}$	
	$\sqrt{1 + (22)^2 + (12)^2} = \sqrt{629}$	$= 25 \text{ ppm.}$
$\frac{e}{m_e c}$	$= \gamma'_p \frac{\omega_e}{\omega'_n} = (1.75889 \pm .00004) \cdot 10^7 \text{ emu/g}$	
$\frac{e}{m_p}$	$= e \gamma'_p \frac{\omega_e}{\omega'_n} = (2.87185 \pm .00009) \cdot 10^{14} \text{ esu/g}$	
	$\sqrt{1 + (22)^2 + (22)^2} = \sqrt{969}$	$= 31 \text{ ppm.}$
$\frac{e}{m_e c}$	$= \gamma'_p \frac{\omega_c}{\omega'_n} = (9579.4 \pm 0.3) \text{ emu/g}$	
	$\sqrt{(22)^2 + (22)^2} = \sqrt{968}$	$= 31 \text{ ppm.}$

TABLE IX (continued).

$\mu_D = \frac{\omega_n'}{\omega_e} \frac{\gamma_D}{\gamma_D'} = (2.79275 \pm .00006) \text{ nuclear magnetons}$	$= 22 \text{ ppm.}$
$\mu_D = \frac{\alpha^5 e}{2(4\pi R)^2 \gamma_D' (\omega_e'/\omega_n')} \cdot \frac{\gamma_D}{\gamma_D'} = (1.41047 \pm .00005) \cdot 10^{-23} \text{ erg G}^{-1}$ $\sqrt{(15)^2 + 1 + (22)^2 + (24)^2} = \sqrt{1285}$	$= 36 \text{ ppm.}$
$\mu_0 = \frac{\alpha^5 e}{2(4\pi R)^2 \gamma_D' (\omega_e'/\omega_n')} = (.927324 \pm .000026) \cdot 10^{-20} \text{ erg G}^{-1}$ $\sqrt{(15)^2 + 1 + (22)^2 + (12)^2} = \sqrt{854}$	$= 29 \text{ ppm.}$
$\frac{h}{e} = \frac{\alpha^2}{2R\gamma_D' (\omega_e'/\omega_n')} = (1.37943 \pm .00003) \cdot 10^{-17} \text{ erg s esu}^{-1}$ $\sqrt{(16)^2 + (22)^2 + (12)^2} = \sqrt{664}$	$= 26 \text{ ppm.}$

quite clear that reduction of the uncertainty in our knowledge of the resonance constants would lead to corresponding improvement in our knowledge of N , e , h , m_e , m_p , μ_0 , μ_D . It is also clear that γ_D' and all that derives from it cannot be refined much further without improved knowledge of the absolute ampere and, as things now stand, of the transfer constant g .

In each case, the numbers under the square root sign indicate the ppm errors associated with each term of numerator then denominator reading left to right, (the 0.1 ppm error in R_∞ is not included). In this approximate way, one sees how the errors in our knowledge of the resonance constants affect values for the physical constants determined with their use. In each instance, the error quoted by the author is used instead of an estimated probable error.

The faraday. — The faraday Ne/c has been determined at NBS both by electrochemical means and by purely physical methods.

The physical determination is based upon the relation

$$F = Ne/c = \gamma_D' (\omega_e'/\omega_n') M_p$$

and follows directly from the determination of

$$\gamma_D', \text{ TDH [28]} \quad \text{and} \quad \omega_e'/\omega_n', \text{ STH [33]}$$

and the value of M_p' as derived from mass spectroscopic measurements [22].

STH report the value

$$F = (9652.0_3 \pm 0.3) \text{ emu/equivalent (physical scale).}$$

Using the value $M_p = (1.007597 \pm 0.000001)$, BT [22] and the reported values for γ'_p and ω_s/ω_n , the value

$$F = (9652.18 \pm 0.3) \text{ emu/equivalent (physical scale)}$$

is obtained (*). The principle sources of error are those in γ'_p and ω_s/ω_n , already referred to. Further work on the physical determination of the faraday is now in progress at NBS, in the form of an improved determination of γ'_p , as has been mentioned.

The electrochemical determination of the faraday is based upon the equation

$$F = Ne/c = (It/M_0)(E_1 + r_2E_2 \dots r_kE_k)/(p_1 + r_2p_2 \dots r_kp_k),$$

where $E_1 \dots E_k$ are the molecular weights of the *ions* involved in the deposition in atomic mass units (physical scale); $r_1 \dots r_k$ are the relative abundances of each as they deposit on the electrode (or dissolve); $p_1 \dots p_k$ are the number of unit charges carried by each ion; I is the current in emu, t the time of current flow, and M_0 the mass transferred. Usually precautions are observed to insure that only one process is involved, so that the above equation is simplified, and we are concerned with the molecular weight of the single ionic species (perhaps of several isotopic constituents) on the physical scale. Thus

$$F = Ne/c = ItE/pM_0.$$

The measurement of the current in terms of the standard ampere and the time, t , can easily be done with accuracy far in excess of that with which the other quantities may be measured. The integer p is, of course, known for the reaction. The uncertainty in F will thus be primarily determined by the errors in the absolute ampere, E , the molecular weights, and M_0 , the mass transferred. The uncertainty in the standard ampere has already been discussed. There remain the errors in the measurement of M_0 and the determination of E on the physical scale. Uncertainties in M_0 arise from inclusions in the deposit or some redissolving of the deposit, in addition to the difficulties in precision weighing. Uncertainties arise in E from impurities which require

(*) This later value was reported by SOMMER and HIPPLE, NBS Circular 524, p. 25 (1953). The change was brought about by improved knowledge of the value of M_p .

corrections to the mass measurements and may lead to other species being involved in the reaction, whose E_i and r_i are not known well enough, as well as the usual errors in the chemical determination of E .

The faraday has been determined several times at NBS. The earlier determinations are confusing, because in those days the «international» ampere was the accepted standard for measurement of electric current, and this was defined in terms of the electro-deposition of silver by a silver voltameter. The international ohm was defined in terms of a column of mercury, and the international volt, on a provisional basis, was independently defined by a standard cell, an apparent redundancy.

Thus, any determination of the international ampere in terms of the absolute ampere became *per se*, an absolute determination of the faraday, if the atomic weight of silver is known and if the voltameter precisely obeys Faraday's law. By accepting the international ohm and the provisionally defined international volt as standard (standard cell = 1.0184 V), it was possible to measure the faraday in international units in terms of these standards.

The conditions for silver depositions by the voltameter, as prescribed by international agreement, were specific and did not take into account processes of redissolving of the deposit or any of the sources of error in an accurate determination of the faraday, as described above, but nevertheless gave a highly reproducible standard of current. Thus, the total charge passing through a circuit could be measured in international coulombs by the silver voltameter. If, then, this same charge could produce electrolytic deposition of silver or some other substance under ideal conditions where perturbing processes were reduced to a minimum, a value of the faraday in international units could be obtained in terms of the standard of current set by the silver voltameter.

The first determination of the absolute ampere at the Bureau was performed in 1911 by ROSA, DORSEY, and MILLER [37], using a current balance. From it, they derived a value for the electrochemical equivalent of silver which they gave as 1.11804 mg per coulomb. Taking the atomic weight of silver as 107.88, an accepted value in those days, leads to an absolute value for the faraday of 9649.0 emu per equivalent. Later VINAL and BATES [38] determined the faraday in international units with an iodine voltameter, using a silver voltameter as a standard of current. They arrived at the value 96514 *international coulombs* per equivalent. The corresponding value for silver would be $107.88/.00118 = 96494$ giving a mean of 96504 based on both silver and iodine. Sources of error in the silver voltameter were subsequently explored [39].

G. W. VINAL recomputed the old determination on the basis of 1949 values for atomic weights and conversion factors for absolute electrical units. When these are corrected to the 1951 atomic mass for iodine and silver, the values

become [40]

Iodine $F = (9652.15 \pm 0.13)$ emu/equivalent (physical scale),

Silver $F = (9651.29 \pm 0.19)$ emu/equivalent (physical scale).

A later determination of the faraday by CRAIG and HOFFMAN [41] by evolution of carbon dioxide from a solution of sodium oxalate, gave a value of 9651.8 emu/per equivalent to which an error of 31 in 10^6 was assigned (*).

At the present time, the NBS is engaged in a new determination based upon both the oxalate and silver methods. The oxalate determination awaits the preparation of some adequately pure oxalate free from inclusions in the crystals.

The silver determination[†] will be made by a new method using perchloric acid. The amount of silver plated off a sample will be determined instead of the amount plated on. It has already been shown that the concentration can be adjusted so that the amount of silver dissolved by the acid will probably be negligible in the process. The point should be settled soon.

The atomic weight of silver based upon chemical determinations is known [42] with a probable error in the precision of about 3 parts in 10^6 and an estimated accuracy [43] of about 20 parts in 10^6 . There seems little likelihood of much improvement. The isotopic masses of the two silver isotopes are known with adequate precision, but the uncertainty in the relative abundance r is such that the physical determination of the atomic weight has an estimated uncertainty [22] of 100 in 10^6 . Until r can be determined with adequate precision, the relation $E = (E_1 + r_2 E_2)/(1 + r_2)$ is of no help. It should also be remembered that r is the ratio «as plated». The mass spectroscopic ratio can be used only if the plating is known to be non-selective.

The silver to be used for the new NBS determination has already been obtained and purified. Analysis for impurities is now in process. Some of it has been set aside for a precision determination of r as soon as the state of the art permits. In the meantime, a value for F based upon the chemical determination of E can be obtained and corrected later when r is known.

These two values of the faraday are not independent but are correlated through a common dependence on the ampere which affects both in the same way and by a dependence on g which affects them differently in an interesting way as shown in the Appendix.

(*) Correcting for the values of the atomic weights. E. WICHERS: *Journ. Am. Chem. Soc.*, **76**, 2033 (1954), reduces this value to 9651.1.

4. - Conclusion.

In assembling the material for this paper, we have attempted to be representative rather than comprehensive. Much work of the Bureau deals with physical constants directly or indirectly. We have completely omitted mentioning, for example, the Bureau's program on temperature measurements. Pleasingly enough, temperature is one of the primary standards which is already defined in terms of physical constants—the triple point of water, $273^{\circ}.16$ and absolute zero. The problem is to determine various other internationally accepted fixed-point temperatures in terms of the thermodynamic scale as defined above.

We have pointed out the desirability and the difficulty of defining certain primary standards in terms of physical constants. We have shown how, willy-nilly, various physical constants are being measured in terms of better-known physical constants, and through them are related to our primary prototype standards.

The science of measurement has now progressed to the stage when serious consideration is being given to defining at least two of our prototype standards, the meter and the second, in terms of physical constants so that they become independently reproducible standards.

It should be stressed that there is no plan to change the value of the meter or to replace present material standards where they are useful, but merely to so define it that more precise measurements can be made with reference to it in those fields where the new definition is more applicable. The situation is not quite the same with the second for, as has been pointed out, the civil or mean solar second is not a constant unit, and the more constant unit, the ephemeris second which would be defined in terms of a physical constant, can be obtained only from lengthy observation. For convenience, the second of civil time, of which there are 86400 in a mean solar day, is a much more useful standard for the average man than the ephemeris second which is now scientifically defined and which differs from the civil second by a measurable amount.

While we think of the prospect of defining standards in terms of physical constants, a thought which was in the minds of scientists even in AVOGADRO's time, we must pause and consider what can be done about the primary standard of mass [45]. We see no hope, at the present stage of our science, to define the standard of mass with sufficient precision in terms of the natural standard, the mass of some chosen elemental particle, atom, or molecule. Neither can we be hopeful of precisely assembling a given number of them, say Avogadro's number, so that the mass of the assemblage may be compared precisely with

the kilogram. The urge to express all of our primary standards in terms of physical constants leads us to examine the roll of mass as one of our standards.

The concept of mass, or more exactly weight, as one of the fundamental standards of measurement, dates back to the dawn of civilization. The concept of mass became clearer with the development of the science of mechanics in the century before AVOGADRO's. Since that time, physical science has progressed greatly, and concepts of quantities then not known have come into being. Important among these quantities, from both the scientific and the practical point of view, are the electric standards.

To relate these electrical standards to our prototype primary standards involves an experimental procedure which cannot be performed at present with the desired accuracy.

We consider, therefore, the advisability of adopting some other primary standard, involving mass dimensionally and deriving the standard of mass from it as a secondary standard. If this were done, we should find ourselves in the same type of difficulty in that the standard of mass could not be determined at the present time with desired accuracy, because of the experimental procedure involved. It seems, therefore, more advantageous to go directly to a four standard system by defining a fourth independent standard in terms of a physical constant which is precisely related to one of the electric quantities, say the ampere. If we do this, then in the MKSA system (meter, kilogram, second, ampere), the permeability of free space μ_0 has a value which is not exactly 10^{-7} (or $4\pi \cdot 10^{-7}$ in the rationalized system) as now implicitly defined, but rather some value close to it which must be determined by experiment. Thus, the permeability of space μ_0 , not the ampere, is the value which must be determined experimentally, and the current balance experiment becomes a determination of μ_0 .

The gyromagnetic ratio of the proton γ_p might supply the basis for just such a standard. We would then define the ampere as the current flowing in an infinite solenoid of n turns per meter which would produce a proton resonance of p cycles per second.

The implications of this suggestion are too extensive to consider in this paper. It cannot be regarded yet as a proposal, because the precision experiments to demonstrate its feasibility are yet to be performed, but we believe that by our present experimental techniques, we can perform the measurements with sufficient precision.

Thus, the gyromagnetic ratio of the proton is one of the physical constants which has taken on a great importance. It is both an important link in our involved chain of physical constants, as shown before, and a possible basis for a revised system of standards. Only one determination of its value has been performed in a laboratory specializing in precision measurements and having direct access to national standards. It is highly desirable that additional

precise determinations of this important constant be performed either by or in close co-operation with the great national standardizing laboratories of the world.

* * *

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APPENDIX

The faraday as determined in two ways.

There have been instances where the faraday as measured by physical methods and as measured by electrochemical methods have been considered to be independent determinations and treated as such. Actually both involve the measured value of g , the acceleration of gravity, and are therefore correlated. The nature of this relation is interesting.

We let F_p be the value of the faraday, *as reported* when determined by physical methods. Similarly, let F_e represent the reported value based upon an electrochemical determination. Both, of course, involve the ampere. The ampere I is a current which is established with an ampere balance through the relation

$$I = \sqrt{\frac{m_1 g}{k_1}},$$

where k_1 is a geometric constant of the balance, and m_1 is the mass used to balance the force due to the current. k_1 is established so that the current thus defined will be the absolute ampere when the balancing mass is m_1 .

To measure the magnetic field used in the determination of γ'_p a current $i = NI$ where N is a pure number is passed through a coil of known dimensions (k_2) and the force measured by balancing it with a mass m_2 . Thus

$$m_2 g = k_2 i H = k_2 N H \sqrt{\frac{m_1 g}{k_1}}.$$

But

$$\gamma'_p = \frac{\omega'_n}{H} = \frac{\omega'_n k_2 \sqrt{m_1 g / k_1} N}{m_2 g},$$

and

$$F_p = M_p \left(\frac{\omega_c}{\omega_n} \right) \frac{\omega_c}{\omega_n} = \frac{M_p (\omega_c / \omega_n) \omega_n' k_2 \sqrt{m_1 g / k_1} N}{m_2 g}.$$

If we assume we do not know g , all the rest of the right hand side is known by the measurements made. Thus, we can write

$$F_p = \frac{P}{\sqrt{g}}.$$

Now

$$F_e = \frac{A}{m_3} it = \frac{A}{m_3} nIt = \frac{A}{m_3} nt \sqrt{\frac{m_1 g}{k_1}},$$

where A is the chemical equivalent weight of the material deposited by current $i = nI$ in time t and m_3 is the observed mass of the deposit. All are known except g so we write

$$F_e = Q \sqrt{g},$$

where Q is a known measured number. Now the values of F_p and F_e reported by the National Bureau of Standard involve the value of g at Washington which may be in error, so we write them indicating Washington values. Thus

$$(F_p)_w = \frac{P}{\sqrt{g_w}},$$

$$(F_e)_w = Q \sqrt{g_w}.$$

Let us suppose that g_w is in error but that the true value of g is g_c . Then the reported values $(F_p)_w$ and $(F_e)_w$ will not agree no matter how accurately the numbers P and Q are measured. If we used the correct value of g we could write

$$F_p = \frac{P}{\sqrt{g_c}}$$

and

$$F_e = Q \sqrt{g_c}.$$

But these two values of the faraday should be the same if no errors are made in P or Q . We are concerned here only with g so we assume that P and Q are correct. Then

$$\frac{P}{\sqrt{g_c}} = Q \sqrt{g_c}$$

$$\frac{P}{Q} = g_c = \frac{\sqrt{g_w} (F_p)_w \sqrt{g_w}}{(F_e)_w} = \frac{g_w (F_p)_w}{(F_e)_w},$$

or

$$\frac{(F_p)_w}{(F_e)_w} = \frac{g_e}{g_w}.$$

We see that whatever value of g_w is used, the reported values $(F_p)_w$ and $(F_e)_w$ will be such that the true value of g can be determined. It is not even necessary to know a value of g ; one can be assumed for purposes of computation.

Since

$$g_e = g_w \frac{(F_p)_w}{(F_e)_w},$$

we can write

$$F^2 = Q^2 g_e = Q^2 g_w \frac{(F_p)_w}{(F_e)_w} = \frac{(F_e)(F_p)_w}{(F_e)_w},$$

$$F^2 = (F_e)_w (F_p)_w,$$

i.e., the true value F , of the faraday which must be independent of the method of measurement is given by

$$F = \sqrt{(F_e)_s \cdot (F_p)_s},$$

where both F_e and F_p are measured at the same gravity station (s) or are values corrected to the same gravity station.

Now the errors in F_e and F_p involve the errors in g at the station but $\sqrt{(F_e) \cdot (F_p)}$ does not. The product should therefore give a better value than either alone. The latest National Bureau of Standards' values are

$F_p = 9652.18$	(Corrected for best value of M_p)	30 ppm,
$F_e = 9651.1$	(Corrected for best value of N_a)	30 ppm,
$F = 9651.64$		21/x ppm,

where $x \sim 1 + \frac{1}{2}(E_g/E)^2$ where E_g is the error contributed by error in g and E is the error from the other sources in both the physical and chemical determinations, provided, as seems to be the case that the E_g is smaller than E .

The correction to g_w that one would deduce would be $g_e = g_w (1.000108 \pm .000042)$. This makes it appear that the g_w is too small but the uncertainty is such that not much faith can be put in the observation. Nor is there any serious belief that g_w is off by more than 10 to 15 ppm.

REFERENCES

- [1] J. BABINET: *Ann. Chim. Phys.*, **40**, 177 (1829).
- [2] J. C. MAXWELL: *Rep. Brit. Ass., Not. and Abstr.*, **7** (1870).
- [3] A. A. MICHELSON and E. W. MORLEY: *Am. Journ. Sci.*, **38**, 181 (1889).

- [4] A. A. MICHELSON: *Trav. Mem. Bur. International Poids Mesures*, **11** (1893); J. R. BENOÎT and E. GUILLAME: *Annexe*, **1** (1893).
- [5] B. L. PAGE: *Journ. Research NBS*, **54**, 1 (1955), R. P. 2559; also L. V. JUDSON and B. L. PAGE: *Journ. Research NBS*, **13**, 757 (1934), R. P. 743.
- [6] K. G. KESSLER: personal communication.
- [7] C. G. PETERS and W. B. EMERSON: *Journ. Research NBS*, **44**, 419 (1950), R. P. 2089.
- [8] W. MARKOWITZ: *Astron. Journ.*, **102**, 171 (1955).
- [9] W. MARKOWITZ: *Res. Rev.*, *ONR*, (U. S. Dept. Navy) (Sept. 1955).
- [10] J. E. SHERWOOD, H. LYONS, R. H. MCCracken and P. KUSCH: *Bull. Am. Phys. Soc.*, **27**, (1), 43 (1952).
- [11] L. ESSEN and J. V. L. PARRY: *Nature*, **176**, 280 (1955).
- [12] R. W. CURTIS, R. L. DRISCOLL and C. L. CRITCHFIELD: *Journ. Research NBS*, **28**, 133 (1942) R. P. 1449; also H. L. CURTIS, R. W. CURTIS and C. L. CRITCHFIELD: *Journ. Research NBS*, **22**, 485 (1939) R. P. 1200.
- [13] R. L. DRISCOLL: *Bull. Am. Phys. Soc.*, **33**, 24 (1955). In this reference the result with the Pellat balance is stated to differ by 19 in 10^6 from other NBS determinations. This figure has since been revised.
- [14] F. B. SILSBEE: *NBS Circular* 475 (1949).
- [15] H. L. CURTIS: *Journ. Research NBS*, **33**, 235 (1944) R. P. 1606.
- [16] J. L. THOMAS, C. PETERSON, I. L. COOTER and F. R. KOTTER: *Journ. Research NBS*, **43**, 291 (1949) RP 2029.
- [17] H. L. CURTIS, C. MOON and C. M. SPARKS: *Journ. Research NBS*, **21**, 375 (1938) RP 1137.
- [18] F. KÜHNEN and P. FURTWÄNGLER: *Pub. Königl. Preussische Geodätische Institute* (1906).
- [19] H. L. DRYDEN: *Journ. Research NBS*, **29**, 303 (1942) RP 1502.
- [20] P. R. HEYL and G. S. COOK: *Journ. Research NBS*, **17**, 805 (1936) RP 946.
- [21] E. B. ROSA and N. E. DORSEY: *Bull. NBS*, **3**, 433 (1907).
- [22] J. A. BEARDEN and J. S. THOMSEN: *A Survey of Atomic Constants* (Baltimore, Md. Johns Hopkins University, 1955).
- [23] E. F. FLORMAN: *Journ. Research NBS*, **54**, 335 (1955) RP 2597.
- [24] E. K. PLYLER, L. R. BLAINE and W. S. CONNOR: *Journ. Opt. Soc. Am.*, **45**, 102 (1955).
- [25] O. R. GILLIAM, C. M. JOHNSON and W. GORDY: *Phys. Rev.*, **78**, 140 (1950).
- [26] F. D. BEDARD, J. J. GALLAGHER and C. M. JOHNSON: *Phys. Rev.*, **92**, 1440 (1953).
- [27] L. E. BERGSTRAND: *Ark. f. Phys.*, **2**, 119 (1950); **3**, 479 (1951).
- [28] H. A. THOMAS, R. L. DRISCOLL and J. A. HIPPLE: *Journ. Research NBS*, **44**, 569 (1950) RP 2104.
- [29] H. A. THOMAS: *Phys. Rev.*, **80**, 901 (1950).
- [30] F. KIRCHNER and W. WILHELMY: *Z. Naturforsch.*, **10**, 657 (1955).
- [31] G. LINDSTROM: *Ark. f. Phys.*, **4**, 68 (1952).
- [32] J. H. GARDNER and E. M. PURCELL: *Phys. Rev.*, **76**, 1262 (1951).
- [33] H. SOMMER, H. A. THOMAS and J. A. HIPPLE: *Phys. Rev.*, **82**, 697 (1951).
- [34] F. BLOCH and C. D. JEFFRIES: *Phys. Rev.*, **80**, 305 (1950).
- [35] K. R. TRIGGER: *Bull. Am. Phys. Soc.*, **31**, (4), 220 (1956).
- [36] D. J. COLLINGTON, A. N. DELLIS, J. H. SANDERS and K. C. TURBERFIELD: *Phys. Rev.*, **99**, 1622 (1955).
- [37] E. B. ROSA, N. E. DORSEY and J. M. MILLER: *Bull. NBS*, **8**, 269 (1912) RP. 171
- [38] G. W. VINAL and S. J. BATES: *Bull. NBS*, **10**, 425 (1914).

- [39] G. W. VINAL and W. M. BOUVARD: *Bull. NBS*, **13**, 147 (1916); E. B. ROSA and G. W. VINAL: *Bull. NBS*, **13**, 479 (1916-17).
- [40] J. W. M. DUMOND and E. R. COHEN: *Rev. Mod. Phys.*, **25**, 691 (1953).
- [41] D. N. CRAIG and J. I. HOFFMAN: *NBS Circular* 524, p. 13 (1953).
- [42] O. HÖNIGSCHMIDT, E. ZINTL and P. THILO: *Zeits. anorg. allgem. Chem.*, **163**, 65 (1927).
- [43] E. WICHERS: personal communication.
- [44] J. R. WHITE and A. E. CAMERON: *Phys. Rev.*, **74**, 991 (1948).
- [45] R. D. HUNTOON and U. FANO: *Nature*, **166**, 167 (1950).

Avogadro's Constant, Loschmidt's Constant, and the Mole (*).

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1. - Definition and meaning of Avogadro's and Loschmidt's constants.

According to the etymologic origin of the word «specific»—quod facit speciem—specific quantities characterize a substance. For a body of mass m , consisting of N equal molecules, the quotient *

$$(1) \quad N_m = \frac{N}{m} = \frac{1}{\mu}$$

is a specific quantity, which is called *specific molecule number*, and which is equal to the reciprocal value of the mass of a molecule, μ . Measuring mass in grams, N_m has a numerical value, characteristic of each kind of molecules. However, using instead of the gram the mass quantities «grammole» («g-mole») defined by equation

$$(2) \quad \text{g-mole} = M^* \text{ g} \quad (M^*: \text{molecular weight}),$$

the numerical value of the specific molecule number becomes independent of the kind of molecules; we denote this universal number by

$$(3) \quad n_m = \{N_m\}_{\text{g-mole}}^{-1}.$$

In the representation

$$(4) \quad N_m = n_m \text{ g-mole}^{-1}$$

too, the specific molecule number is still to be considered as specific quantity, however, here it is not the numerical value n_m that is specific for the substance,

(*) [In questo articolo sono stati usati, in alcuni casi, simboli diversi da quelli usati, negli altri scritti di questo stesso fascicolo, per indicare le medesime quantità (N. d. R.).]

as generally customary with specific quantities, but the used «unit» g-mole [42]. In the definition (2) the grammole does not represent a mass unit but mass quantities, which vary from substance to substance according to their molecular weight. Dealing with the kinetic and thermodynamic behaviour of gases, there is, besides the specific molecule number N_m referred to mass, another quantity of interest, related to the gas volume, v ,

$$(5) \quad N_v = \frac{N}{v},$$

which is called *molecule number density* and connected with the specific molecule number by the density $\rho = m/v$ or by the specific volume $v_m = 1/\rho$ through the relationship

$$(6) \quad N_v = \frac{m}{v} N_m = \rho N_m = \frac{N_m}{v_m}.$$

In the special case of a perfect gas at standard temperature and pressure (S.T.P.: $p_0 = 1$ atm, $T_0 = 273.15^\circ\text{K}$; see Sect. 5) the molecule number density can be associated with the specific volume of the perfect gas at S.P.T., v_{m_0} , by the equation

$$(7) \quad N_{v_0} = \frac{N_m}{v_{m_0}} = L_0.$$

According to the hypothesis of AVOGADRO, L_0 is independent of the special kind of «ideal» gas molecules and therefore a constant characteristic of ideal or perfect gases; its numerical value, measured in cm^3 ,

$$(8) \quad l_0 = \{L_0\}_{\text{cm}^3}$$

is equal to the number of gas molecules which are contained in the volume 1 cm^3 of a perfect gas at S.T.P.

In the representation of equation (4) N_m is related, contrary to L_0 , to the definition of the grammole. n_m is equal to the number of molecules «in one mole», yet the conceptions how to define suitably «1 mole» differ still. We shall revert to this in Sect. 3; however, we shall first of all deal with a quantity

$$(19) \quad N_0 = N/Q,$$

which is defined in analogy to the specific molecule number, N_m , and which, corresponding to equation (4), can be written

$$(9) \quad N_0 = n_0 \text{ mole}^{-1};$$

here, contrary to the mass quantities g-mole of equation (2), the mole appearing is a unit of « quantity of substance » Q (see Sect. 3).

Unfortunately, the designation and nomenclature for the four quantities or numerical values N_0 , n_0 , L_0 , l_0 is not uniform. Side by side and also mixed up they are: as well on one hand designated as « constant » and « number » as on the other hand associated with the names « Avogadro » and « Loschmidt ».

Since N_0 and L_0 are no pure numbers but dimensional quantities independent of the choice of units, they should not be called numbers but constants. The numerical values n_0 and l_0 , however, depend on the units used for N_0 and L_0 and should consequently be called numbers; here one should still try to attain an agreement about the reference units, e.g. mole⁻¹ for n_0 and cm⁻³ for l_0 .

At present two co-ordinations are in use with the names AVOGADRO and LOSCHMIDT: on one side $N_0 = \text{Avogadro's constant}$ and $L_0 = \text{Loschmidt's constant}$ and on the other side vice versa $N_0 = \text{Loschmidt's constant}$ and $L_0 = \text{Avogadro's constant}$.

AVOGADRO [1] based 1811 his hypothesis mainly on Gay-Lussac's volume law: his arguments do not deal with the homologous reaction of gases against changes of pressure and temperature, but are related to the distances of gas molecules between each other under certain equal conditions. To this fact OSTWALD [2] referred explicitly. AVOGADRO formulated his hypothesis:

« L'hypothèse qui se présente la première à cet égard, et qui paroît même la seule admissible, est de supposer que le nombre des molécules intégrantes dans les gaz quelconques, est toujours le même à volume égal, ou est toujours proportionnel aux volumes. En effet, si on supposoit que le nombre des molécules contenues dans un volume donné fût différent pour les différens gaz, il ne seroit guère possible de concevoir que la loi qui présideroit à la distance des molécules, pût donner, en tout cas, des rapports aussi simples que les faits que nous venons de citer, nous obligent à admettre entre le volume et le nombre des molécules. »

Here the distances between the molecules should, according to the conceptions of his time, correspond to a quasi-static equilibrium, which is caused by the « phlogiston » (« fluide calorique ») imagined around each molecule.

LOSCHMIDT [3] already considered the distance between molecules as a statistical average of a dynamic equilibrium in the kinetic conception of the collisions between freely moving molecules as it was appropriate to the preceding publications of HERAPATH and KRÖNIG, CLAUSIUS, MAXWELL, MEYER, RANKINE etc. LOSCHMIDT evaluated 1865 for the first time a molecule diameter starting with Clausius's formula [4] for the mean free path length

$$(10) \quad \lambda = \frac{3}{4\pi s^2 N_v} \quad (s: \text{molecule diameter})$$

by means of the «condensation coefficient»

$$(11) \quad \varepsilon = \frac{N_0 \pi s^3}{6} = \frac{s}{8\lambda},$$

i.e. the ratio of the N -fold space of one molecule to the gas volume occupied by N molecules: «Der Durchmesser der Moleküle eines Gases ist gleich der achtfachen mittleren Weglänge, multipliziert mit dem Condensationscoefficienten.»

LOSCHMIDT obtained, with the data for λ known at that time and an ε -value estimated by him from the density of liquid and vapour at the boiling point, $1 \cdot 10^{-7}$ cm for the diameter of an air molecule; from this, with the λ -value used by LOSCHMIDT, the molecule number density at S.T.P., $N_{v_0} = L_0$, comes out according to equation (10) as $2 \cdot 10^{18}$ cm $^{-3}$ approximately, thus nearly by the factor 10 too low (see Sect. 5).

As well N_0 as L_0 may be considered as the characteristic constant of Avogadro's hypothesis about the number of gas molecules in a certain volume. However, with the knowledge of molecular properties at that time AVOGADRO could estimate neither for N_0 nor for L_0 the values, not even their order of magnitude. Half a century later LOSCHMIDT was the first to do so. His calculations led directly to the constant L_0 and from this over the mole concept to the constant N_0 . It is because of the quantitative results of LOSCHMIDT's publication that VIRGO [5] wants to associate N_0 and L_0 with the name LOSCHMIDT. However, as these two constants are widely used side by side, they should be unequivocally distinguishable by their designations. The following nomenclature would be appropriate to the historical development and meet the operational definition for physical quantities:

for the constants

N_0 : Avogadro's constant (9/19)

L_0 : Loschmidt's constant (7)

for their numerical values

n_0 : Avogadro's number (3/9)

l_0 : Loschmidt's number (8).

For most cases the numerical values n_0 and l_0 might be superfluous.

Loschmidt's constant L_0 describes the space occupied by molecules of an ideal gas. *Avogadro's constant* N_0 is beyond this a fundamental constant.

independent of the state of aggregation and is of special importance in physics and chemistry. The quotient N_0/L_0 is the *molar volume of perfect gas at standard temperature and pressure*, V_0 (see Sect. 5).

2. - Values for Avogadro's constant.

The values for Avogadro's constant evaluated and recommended in the last ten years can be divided in two groups: (a) N_0 -values from direct experimental determination, and (b) N_0 -values from an analysis of precision measurements of quantities, interlaced with atomic constants, by least-squares adjustment.

(a) *Direct experimental N_0 -determinations.* - In order to measure Avogadro's constant one uses the so-called X-ray-crystal-density method (XRCD method), which starts from the direct application of definition (1) for the specific molecule number, N_m , to crystals. One chooses as « body » the « unit cell » of a sound crystal (the unit cell containing f « molecules » of the crystallized substance), and evaluates the mass m of the unit cell from its roentgenographically determined volume v and the macroscopically measured density ρ of the crystal:

$$(1') \quad N_m = \frac{f}{\rho v}.$$

The volume depends on the crystal system; e.g. there is for cubic unit cells $v = a^3$ (a : lattice constant), for rhombohedral unit cells $v = \Phi(\beta) \cdot a^3$ ($\Phi(\beta)$: geometric function of the rhombohedron angle β), for hexagonal unit cells $v = 3a^2c\sqrt{3}/2$ (a, c : lattice constants).

Lattice constants are according to roentgenographic methods measured in Siegbahn's X-units (symbolic abbreviation XU), i.e. related to the calcite, crystal: its spacing for the cleavage plane or crystal grating constant at 18 °C, $d_{\infty}^{18^\circ}(\text{CaCO}_3)$, defines the XU:

$$(12) \quad d_{\infty}^{18^\circ}(\text{CaCO}_3) \equiv 3019.45 \text{ XU}.$$

As density is macroscopically measured, for instance, in g/cm^3 , the unit cell volume v determined in XU^3 must be converted by the cube of the factor

$$(13) \quad k_\lambda = \frac{1 \text{ XU}}{10^{11} \text{ cm}},$$

into metric units. The *conversion factor* k_λ can be experimentally determined with diffraction gratings and monochromatic X-rays, whose wave lengths in

XU are known with sufficient accuracy. 1947 the X-ray-Analysis Group of the American Institute of Physics and the American Society for X-Ray and Electron Diffraction agreed, with the consent of BRAGG and SIEGBAHN, upon the relation [6]

$$(13') \quad k_A = 1.002\,02 \pm 0.000\,03,$$

which is international widely used since that time.

For Avogadro's number

$$(9/4) \quad n_0 = \frac{N_0}{\text{mole}^{-1}} = \frac{N_m}{\text{g-mole}^{-1}},$$

i.e. a specified numerical value for Avogadro's constant N_0 , one obtains a value by conversion of the density ρ , measured in g/cm^3 (*), into $\text{g-mole}/\text{cm}^3$ according to equation (2) — consequently, the molecular weight M^* of the crystal molecules enters into the determination of n_0 . Molecular weights refer partly to the chemical and partly to the physical scale of atomic weights, hence one distinguishes between a chemical and a physical grammole

$$(2') \quad \text{g-mole}_{\text{ch}} = M_{\text{ch}}^* \text{ g},$$

$$(2'') \quad \text{g-mole}_{\text{ph}} = M_{\text{ph}}^* \text{ g}.$$

For the conversion between both scales «Smythe's factor», k_A , is defined (see Sect. 4) which here is written

$$(27') \quad k_A = \frac{M_{\text{ph}}^*}{M_{\text{ch}}^*} = \frac{\text{g-mole}_{\text{ph}}}{\text{g-mole}_{\text{ch}}} = \frac{\text{mole}_{\text{ph}}}{\text{mole}_{\text{ch}}}.$$

The conversion factor k_A can be evaluated from the measurement of the relative abundance of the stable oxygen isotopes ^{16}O , ^{17}O , ^{18}O , and their isotopic weights. We shall enter particularly into this matter in Sect. 4. Altogether, for a direct N_0 -determination by the XRCd method the parameters f , M^* , ρ , d (and Φ eventually) or a and c are to be known for the crystal.

These considerations are strictly applicable only to a «perfect» crystal [13]. In case of a real crystal its «effective» molecular weight M_{eff}^* must be inserted

(*) ρ is often experimentally determined in g/l . For a conversion into g/cm^3 one uses the relation $1\text{ l} = 1.000028\text{ dm}^3$ recommended by the International Committee of Weights and Measures in 1950 [7].

instead of M^* . Crystals are in general not completely pure, apart from those prepared artificially under special precautions; naturally grown crystals contain impurities of changing composition and concentration, which are distributed throughout the crystal in different ways. In case the crystal has an entirely regular lattice or contains, besides its proper cations, only homologous ions of known origin at cation positions in random distribution throughout the whole crystal (substitutional mixed-crystal), it is still possible to consider the macroscopically measured density ρ as limit of the quotient mass/volume for a crystal volume of unit cell size and to calculate from a chemical analysis of the compound the effective molecular weight M_{eff}^* . However, this is not a priori the case, if the crystal contains vacancies or dislocations, e.g. interstitial atoms in addition to its normal lattice atoms or ions.

It is, further, firstly necessary to verify by experiment the equality of a lattice constant, measured roentgenographically only in the outer molecule layers of the crystal because of the high absorptive power of crystals for X-rays, with the real lattice constant in the interior of the crystal. Secondly the existence of defects in the structure of the crystal, e.g. statistically distributed vacancies and dislocations or other imperfections (e.g. mosaic structure) should be experimentally excluded or their extent quantitatively determined. Although they would not affect a roentgenographically measured lattice constant, the measured macroscopic density would, however, differ from that of the «perfect» crystal, on which is based the relationship (1') for the calculation of Avogadro's constant.

As kind and degree of contamination and lattice imperfection may vary with different samples of a crystalline substance, on principle the parameters M_{eff}^* , ρ , d , (and Φ eventually) or a and c , needed for the N_0 -determination, should be measured at the same sample. This point as well as the importance of the evaluation of the effective molecular weight M_{eff}^* has been emphasized by STRAUMANIS [10].

In Table I are listed several N_0 -values, which have been evaluated since 1945 using different crystals, referring to the chemical (column 6) and to the physical (column 8) scale of atomic weights. The values used by the authors for the conversion factors k_λ and k_A are given in columns 5 and 7. As far as N_0 was not published in $\text{mole}_{\text{ch}}^{-1}$ and $\text{mole}_{\text{ph}}^{-1}$ in the original paper, the corresponding values have been calculated with the proper value for k_A of column 7 and inserted in italic type; with no. 5 the value 1.000279 of relation (30) is used for k_A . As far as necessary, column 5 has been completed by the internationally adopted value (13') $k_\lambda = 1.00202$ (in these cases printed in italic type). Only in a few cases of the N_0 -determinations listed in Table I all needed data of the crystal—effective molecular weight, density, unit cell volume—have been evaluated *at the same sample* of crystals mentioned in column 4. Partly the investigations had been made with another purpose:

TABLE I. — *N*

Item No.	Author	Year	Crystals used
1	BIRGE [8]	1945	Calcite, NaCl, diamond, LiF, K
2	STILLE [9]	1948	Calcite
3a	STRAUMANIS [10]	1949	Calcite with $N'_s = 6.0594 \cdot 10^{23} \text{ m}$
3b			
4	KIRCHNER [11]	1950	Calcite, NaCl, diamond, LiF, K
5	ADDINK [12]	1951	Calcite, diamond, quartz, KCl.
6	STILLE [13]	1952	Calcite, rocksalt, diamond, KCl
7	STRAUMANIS [14]	1953	Calcite with $N'_s = 6.0594 \cdot 10^{23} \text{ m}$
8	STRAUMANIS [15]	1954	Calcite with $N'_s = 6.0594 \cdot 10^{23} \text{ m}$
9	BROGREN [16]	1954	Calcite, quartz
10a	SMAKULA, KALNAJS and SILS [17] .	1955	Si, Al, CaF ₂ , Ge
10b			
11	STILLE (*).	1956	Calcite, rocksalt, diamond, KCl

(*) Here, contrary to the N_0 -determination no. 6 of 1952, the meanwhile recommended international chemical atomic weights [40]: 22.991 for sodium, 12.011 for carbon, and 35.457 for chlorine are used.

e.g. determination of vacancies or dislocations in the crystal lattice by measuring density and lattice parameters, evaluation of the variation of lattice distortions under different external influences on the crystal, determination of molecular weight under the assumption of a standard value for Avogadro's constant, determination of lattice imperfections from the deviation of the individual N_0 -values of crystals from the standard value. STRAUMANIS [10, 14, 15, 18] recommends as standard value the so-called « Siegbahn's » Avogadro's constant N'_s , i.e. the value used by SIEGBAHN [19] for determination of X-ray wave lengths

$$(14) \quad N'_s = \frac{100.075 k_A^3}{M_{\text{ch}}^*(\text{calcite})} N_0 = 6.0594 \cdot 10^{23} \text{ mole}_{\text{ch}}^{-1},$$

which he calculated from Faraday's constant and the « oil drop » value of the elementary charge known at his time. Certainly, N'_s is appropriate for special cases, e.g. in crystallography, but not generally applicable as basic value for Avogadro's constant N_0 .

(b) N_0 -values derived from analysis of the atomic constants. — It is the aim of these investigations to determine, from the entire present information about precision measurements of atomic constants, values for the various quantities, which are most compatible with the observed data and the relationships existing between the quantities, and to state by an appropriate criterion or test, how far the values thus determined still diverge from an « ideal » consistency between each other on the basis of the applied physical laws. For

RCD method.

k_A	N_0 in $10^{23} \text{ mole}_{\text{ch}}^{-1}$	k_A	N_0 in $10^{23} \text{ mole}_{\text{ph}}^{-1}$
30 ± 0.000020	6.02338 ± 0.00043	1.000272 ± 0.000005	6.02502
2 ± 0.00003	6.0231 ± 0.0039	$1.000272_4 \pm 0.000007$	6.0247 ± 0.0040
1.00203	6.02385 ± 0.00030	1.000275	6.02551
1.002020	6.02403 ± 0.00030	1.000272	6.02567
2 ± 0.00003	$6.0235_6 \pm 0.0015$	1.000272 ± 0.000007	6.025267 ± 0.0015
1.00202	$6.0228 (\pm 0.0010)$	1.000279	6.0245
2 ± 0.00003	$6.0236_5 \pm 0.0015$	$1.000279_1 \pm 0.000003$	$6.0253_3 \pm 0.0015$
1.00202	6.02403 ± 0.00025	1.000272	6.02567 ± 0.00026
1.002063	6.02326	1.000272	6.02489 ± 0.00030
1.00202	6.02336	1.000272	6.02500
1.002026	6.02368 ± 0.00002	1.0002783	6.02536
1.002063	6.02301 ± 0.00002	1.0002783	6.02469
2 ± 0.00003	$6.0236_9 \pm 0.0006$	1.000279 ± 0.000003	$6.0253_7 \pm 0.0006$

this purpose, having catalogized all of the known experimental data, some few of the great number of atomic constants, e.g. n constants, are selected as « unknowns ». Then one formulates from m « input data » of high accuracy ($m > n$) m « observational equations »; each of them equates a numerically measured value to a function of the n unknowns. This $(m - n)$ -fold over-determined set of equations is « linearized » adopting « origin values » for the n unknowns which have been chosen sufficiently close to the expected solution. Taking into account the estimated errors of the input data, the linearized system of m equations is solved by the least-squares method. The n adjusted output values form, together with their error matrix and correlation coefficients, the « best compromise » solution, the consistency of the data being checked by the χ^2 -test.

The error sources [24, 25] of this method depend on (i) the difficulty to assign the correct values and weights to the input data, (ii) the impossibility to determine the actual law of error distribution applicable to the data, (iii) the risk of unsuspected systematic errors in the data, which may not be revealed even by various tests of the consistency of the output values. Of course, a least-squares adjustment carried out with the best possible care cannot make erroneously determined data more precise. However, such investigations, which require extended calculations generally only to be performed by electronic computers, have proven, when interpreting cautiously the adjusted values, to be very successful.

In the case of Avogadro's constant there are listed in Table II several of

TABLE II. — N_0 -values by least

Item No.	Author	Year	Unknowns of least-squares adjustment
12	DUMOND and COHEN [20]	1948	F, N_0, h
13	BEARDEN and WATTS [21]	1950-51	F, N_0, h
14	DUMOND and COHEN [22]	1950-51	$N_0, e, m_e, h, c_0, k_\lambda$
15	WITMER [23]	1951	$h/e, R_\infty, c_0, M_p^*$
16	DUMOND and COHEN [24]	1952	$N_0, e, m_e, h, c_0, k_\lambda$
17	DUMOND and COHEN [25]	1953	$\alpha, c_0, e, N_0, k_\lambda$
18	BEARDEN and THOMSEN [26]	1955	e, h, N_0
19	COHEN, DUMOND, LAYTON and ROLLET [27]	1955	$\alpha, e, N_0, k_\lambda$

the N_0 -values analytically determined since 1945. Table II is drafted in analogy to Table I, also regarding the significance of the numbers printed in italic type in columns 5 to 7. Column 4, which contains in Table I the used particular crystals, represents in Table II the particular unknowns of the least-squares adjustment. Tables I and II are *commonly* successively numbered.

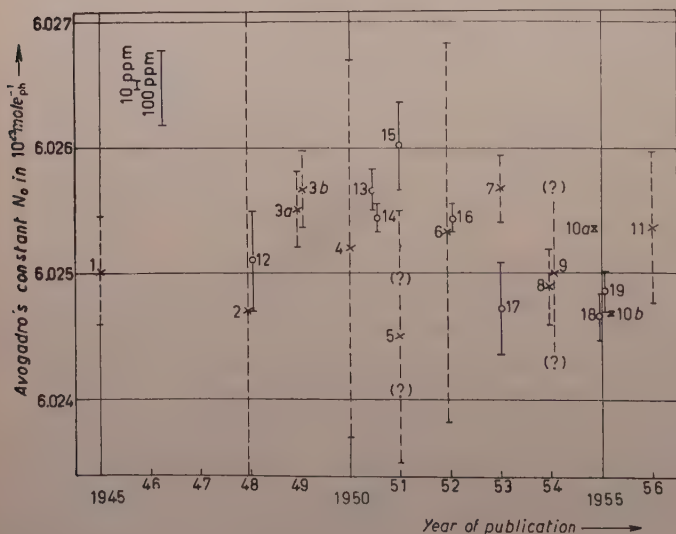


Fig. 1. — Values, since 1945 evaluated for Avogadro's constant N_0 : (a) from direct experimental determination by the X-ray-crystal-density method (x); (b) from least squares adjustment of observational data from precision measurements of atomic constants (o). The numbers beside the crosses and circles indicate the item no., under which the proper publication is listed in Table I or II.

(c) Comparison of « experimentally » and « analytically » determined N_0 -values. — Fig. 1 shows the N_0 -values listed in column 8 of Tables I and II as

ent of atomic constants.

k_A	N_0 in $10^{23} \text{ mole}_{\text{ch}}^{-1}$	k_A	N_0 in $10^{23} \text{ mole}_{\text{ph}}^{-1}$
1.0030 ± 0.000020 (auxil. constant)	6.0235 ± 0.0004	1.000272 ± 0.000005 (auxil. constant)	6.0251 ± 0.0004
1.0030 ± 0.000020 (auxil. constant)	6.02402 ± 0.00017	1.000272 ± 0.000005 (auxil. constant)	6.02566 ± 0.00016
1.00204 ± 0.0000114	6.023800	1.000272 ± 0.000005 (auxil. constant)	6.025438 ± 0.000107
1.00202	6.02433	1.000279	6.02601 ± 0.00035
1.0020 ± 0.000011	6.02380	1.000272 ± 0.000005 (auxil. constant)	6.02544 ± 0.00011
1.0063 ± 0.000034	6.02304_3	1.000279	$6.02472_3 \pm 0.00036$
1.003 ± 0.00002	6.02300_2	1.000275 (auxil. constant)	$6.02465_8 \pm 0.00018$
1.0039 ± 0.000014	6.02318	1.000279	6.02486 ± 0.00016

function of the year of publication, in order to illustrate their mutual situation. The arrows indicate the uncertainty stated by the author for the result (for experimental values with dashes, for analytical values with solid lines). Unfortunately, the error indications are not comparable regarding their derivation and meaning, and therefore they cannot be considered to be a correct measure of the relative accuracy of the particular N_0 -values. For the experimentally determined N_0 -values the errors partly are stated as probable or standard errors, i.e. they represent the statistic variation of the observed data, partly they represent error limits, i.e. they include a judgement about the spread of uncertainty which may occur with the method of measurement. For the analytically determined N_0 -values are probable or standard errors resulting from the least-squares adjustment and depend mainly on the choice of the input data and the estimation of their standard errors. Thus, in Fig. 1 long and short arrows alternate according to the particular kind of error used by the author.

One can, however, state the following. The experimental N_0 of Table I (crosses in Fig. 1) as well as the analytical N_0 of Table II (circles in Fig. 1) show between each other a considerable variability. This also applies to the N_0 published during the last 3 or 5 years; here the experimental N_0 perhaps are in the average somewhat higher than the analytical N_0 — however, they both are still compatible within the estimated error limits. From the nine crystals mentioned in nos. 10 and 11, with the value, at present internationally adopted, $k_A = 1.00202$, would results a mean value

$$(15a) \quad N_0 = 6.0254 \cdot 10^{23} \text{ mole}_{\text{ph}}^{-1},$$

whereas the mean of the two last analytical evaluations of nos. 18 and 19 would be around

$$(15b) \quad N_0 = 6.0248 \cdot 10^{23} \text{ mole}_{\text{ph}}^{-1},$$

with $k_\lambda = 1.00203$ and 1.00204 respectively. The relative difference between both values (15a) and (15b) amounts to $1 \cdot 10^{-4}$; this difference represents only the one- to fivefold of the relative deviations which appear between the N_0 -values published during the last 5 years. Therefore one should use some precaution drawing conclusions from the relative difference of $1 \cdot 10^{-4}$ regarding probable sources of error in the experimental or analytical method as well as regarding the preference of one or the other mean value.

Further we shall discuss the influence of the values mentioned in columns 5 and 7 of Tables I and II for the conversion factors k_λ and k_A . The k_A -values used by different authors deviate from each other at maximum by 0.007% . This variation is of no importance for the N_0 -problem at the moment, as the deviation of the N_0 -values between each other amounts to some $10^{-2}\%$; i.e. we shall obtain the same results using the N_0 -values referring to the chemical scale of atomic weights (column 6) instead of the N_0 -values referring to the physical scale (column 8). Besides, the diminishing of the uncertainty for k_A is limited on principle, the limit being higher than $10^{-2}\%$. We shall revert to this in Sect. 4.

As already emphasized under (a), using the X.R.C.D. method, it is not N_0 that is resulting as directly measured quantity but

$$(16) \quad N'_0 = k_\lambda^3 \cdot N_0.$$

Since in the least-squares adjustment of (b) besides N_0 the conversion factor k_λ can be and is chosen as unknown, where N_0 and k_λ are connected by equation (16), N'_0 can also be important for the evaluation of the analytical N_0 -values.

The N'_0 -values following from the N_0 - and k_λ -values of Tables I and II, referring to the physical scale of atomic weights, are listed in Table III and shown in Fig. 2. N'_0 -values, which contain an italic printed N_0 - or k_λ -value of the Tables I and II, here are also printed in the same type.

A comparison of Figs. 1 and 2 shows that the variability of N'_0 is somewhat smaller than that of N_0 , however, not by an order of magnitude. In particular, there result between the mean of the two last experimental nos. 10 and 11

$$(16a) \quad N'_0 = 6.0620 \cdot 10^{23} \text{ mole}_{\text{ph}}^{-1}$$

and the mean of the two last analytical nos. 18 and 19

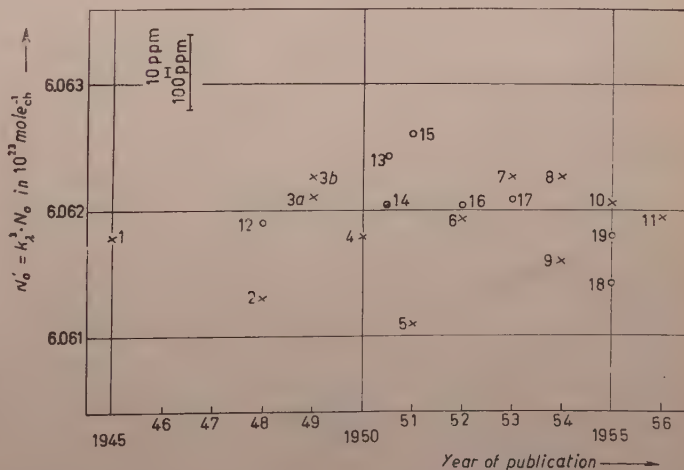
$$(16b) \quad N'_0 = 6.0616 \cdot 10^{23} \text{ mole}_{\text{ph}}^{-1}$$

TABLE III. N'_0 -values by XRCd method and by least-squares adjustment of atomic constants.

Item No.	Author	Year	$N'_0 = k_\lambda^3 \cdot N_0$ in $10^{23} \text{ mole}_{\text{ph}}^{-1}$
1	BIRGE [8]	1945	6.06179
2	STILLE [9]	1948	6.0613
3a	STRAUMANIS [10]	1949	6.06210
3b			6.06226
4	KIRCHNER [11]	1950	6.0617 ₉
5	ADDINK [12]	1951	6.0611
6	STILLE [13]	1952	6.0619 ₂
7	STRAUMANIS [14]	1953	6.06226
8	STRAUMANIS [15]	1954	6.06226
9	BROGREN [16]	1954	6.06159
10a	SMAKULA, KALNAJS and SILS [17]	1955	6.06205
10b			6.06205
11	STILLE (*)	1956	6.0619 ₆
12	DUMOND and COHEN [20]	1948	6.0619
13	BEARDEN and WATTS [21]	1950-51	6.06243
14	DUMOND and COHEN [22]	1950-51	6.062033
15	WITMER [23]	1951	6.06260
16	DUMOND and COHEN [24]	1952	6.06203
17	DUMOND and COHEN [25]	1953	6.06208 ₇
18	BEARDEN and THOMSEN [26]	1955	6.06142 ₃
19	COHEN, DUMOND, LAYTON and ROLLET [27]	1955	6.06179

(*) See footnote (*) to Table I.

Fig. 2. — $N'_0 = k_\lambda^3 \cdot N_0$, the values for Avogadro's constant N_0 and the conversion factor k_λ taken from Table I or II: (a) from direct experimental determination by the X-ray-crystal-density method (x); (b) from least-squares adjustment of observational data from precision measurements of atomic constants (o). The numbers beside the crosses and circles in



indicate the item no., under which the proper publication is listed in Table I or II.

as relative difference $7 \cdot 10^{-5}$ contrasted with $1 \cdot 10^{-4}$ for the corresponding mean values of N_0 (15a) and (15b). From this may be concluded that the uncertainty for k_λ noted in equation (13') with $3 \cdot 10^{-5}$ may not be held alone responsible for the deviations of the N_0 -values. k_λ can be calculated from (15a) and (15b) with 1.00202₁, from (16a) and (16b) with 1.00203₂. Certainly, further experimental work on k_λ is desirable and necessary, but its result probably will not completely eliminate the present discrepancies with N_0 .

On one side, there remains the demand for further and, if possible, still more precise measurements by the XRCd method using sound crystals, where all entering parameters should be determined *at the same sample* and the conversion factor k_λ should be measured anew; quantitative information about the degree of lattice-imperfections should be made accessible by other investigations. Another promising way for the evaluation of Avogadro's constant with higher accuracy will become practicable by means of least-squares adjustment as soon as the further development of special methods for precision measurement of atomic constants will allow to include new experimental results as input data. To this, new determinations of Avogadro's constant by the XRCd method might as well contribute essentially. Here it should be mentioned that at present in the error matrix for the adjusted output values of the unknowns α , c_0 , e , N_0 , k_λ in no. 17 and α , e , N_0 , k_λ in no. 19 (Table II) the resulting errors are the highest just for N_0 . Even in analysis no. 18 with the unknowns e , h , N_0 the resulting error for N_0 reaches nearly that for h .

The result of the above discussed N_0 -determinations may cautiously be summarized as follows: The true value of Avogadro's constant will be found around

$$(15c) \quad N_0 = 6.0250 \cdot 10^{23} \text{ mole}_{\text{ph}}^{-1}$$

and will probably not differ from this value by more than several 10^{-2} ‰ .

3. - The mole.

The until now most usual interpretation of the «mole» has already been mentioned in Sect. 1: the mass quantities g-mole of equation (2). They are defined in order to enable us to deal with and fix mathematically the laws governing *atomic processes*, as they exist in chemical reactions, in a *formally* simple way and in a representation suitable for a *continuum-theoretical description of macrophysics*, without introducing new concepts or fundamental quantities appropriate to atomistics. Instead of counting the single atoms or molecules as individuals, one starts from their property of having mass, which is characteristic of the kind of the respective atoms or molecules. The counting of the single individuals equal between each other is replaced in the description

of the processes and states of chemically uniform bodies, treated as being a continuum, by the introduction of special mass quantities, which are individually defined for every body in such a way that they all are containing *equal numbers of molecules*. Corresponding to the considered body the mass quantities grammole represent different masses; consequently the grammole is surely no mass unit [42].

An objection, often made against the definition and the use of the mole as mass quantity, is the fact, that in atomic processes the *mass* of atoms or molecules mostly is not so important as the fact of their individual existence or their *number*.

Therefore, a new quantity Q , which we will call *quantity of substance*, is introduced. According to definition Q corresponds to the property of matter to consist of single individuals—e.g. in the case of chemically uniform bodies of equal atoms or molecules—and is proportional to the number of these individuals. The quantity of substance is not derived from customary quantities of mechanics but is considered as a new fundamental or basic quantity [28, 42].

Using quantity of substance as reference quantity one can define a new group of specific quantities, e.g. for a body with mass m , volume v , and quantity of substance Q , the quantities

$$(17) \quad \text{molar mass} \quad M = \frac{m}{Q},$$

$$(18) \quad \text{molar volume} \quad V = \frac{v}{Q}.$$

As quantity of substance is introduced as an independent kind of quantity, a unit, suitable for its measurement, cannot be derived from other units but must be defined as a new fundamental or basic unit. The amount of such a unit for the quantity of substance should be chosen as being equivalent to the concept of the mass quantities grammole.

As already stated in Sect. 1, one grammole contains independent of the considered body an equal number of molecules, $n_m = n_0$, i.e. Avogadro's number. If the quantity of substance unit, $[Q]$, which is proportional to the number of molecules contained in it, shall correspond to the grammole, one could easily fix $[Q]$ as the quantity of substance of an arbitrary chosen body, which contains n_0 molecules,—i.e. connecting the $[Q]$ -definition with the numerical value of Avogadro's constant. However, this consideration seems to be illusionary remembering the result of Sect. 2 about the accuracy with which Avogadro's constant is known to-day. It would be unsuitable to base the new unit for quantity of substance on a numerical value which is uncertain by some $10^{-2} \%$, whereas in the physical scale of atomic weights isotopic weights can be determined with an accuracy higher by one power of ten. In this case it would be

necessary either to adjust the defining amount of $[Q]$ at every variation or amendment of the value n_0 or to renounce a numerical fixation of the defining molecule number. The second alternative would be equivalent to a definition of the new unit $[Q]$ over a fundamental constant, which at each time must first be determined and which at present can only be evaluated with a considerable uncertainty.

Therefore it seems more appropriate to the situation to look for an étalon or standard for $[Q]$ which can be unambiguously defined. For this purpose one can choose bodies, which contain equal individuals and whose quantity of substance can directly or indirectly be exactly defined—e.g. bodies consisting of equal atoms or molecules. The quantity of substance, which should correspond to the mass quantities grammole, can be correlated over the molar mass M of equation (17) to a suitably chosen value for the mass m of the « standard body ».

Since a long time atoms are used as standard bodies for atomic weight scales, i.e. relative mass scales. In principle in these scales relative mass, i.e. the molecular weight M^* appearing in equation (2) for the mass quantities grammole, is defined as the ratio: mass of the considered molecule divided by the mass of a standard atom. To-day one is using as standard atom in the chemical scale the « natural » oxygen atom \bar{O} , i.e. atomic oxygen as mixture of the stable isotopes ^{16}O , ^{17}O and ^{18}O corresponding to their average abundance ratio found in nature, and in the physical scale the oxygen isotope ^{16}O . In order to adjust the present scales numerically as far as possible to previous scales of atomic weights, one did not fix as denominator of the ratio M^* the mass of the standard atom \bar{O} and ^{16}O respectively, but its sixteenth part. Hence \bar{O} is to be considered as standard for the chemical molecular weights M_{ch}^* and consequently, according to equation (2'), also for the mass quantities g-mole_{ch}; and in analogy ^{16}O is to be considered as standard for the physical molecular weights M_{ph}^* and the mass quantities g-mole_{ph} of equation (2'').

Obviously, one will achieve the equivalence between the grammole and the new quantity of substance unit, $[Q]$, most easily by choice of \bar{O} or ^{16}O as *primary standard* for $[Q]$. As there exist the above mentioned principle uncertainties in the chemical scale of atomic weights, with which we shall deal quantitatively in the following section, one should prefer the oxygen isotope ^{16}O .

Consequently the quantity of substance unit, $[Q]$, which we will call *mole*, should be defined as follows: 1 mole is the quantity of substance of a body containing as many equal individuals (molecules, atoms, ions, radicals, etc.) as oxygen isotopes ^{16}O are contained in exactly 16 g oxygen (*).

(*) Here a suitable completion or extension of this definition to elementary particles, free valences and photons (e.g. gramequivalent and val.) shall be disregarded.

The quantity of substance Q of a body and the number N of molecules contained in it are proportional. As proportionality factor there appears a fundamental constant, which is Avogadro's constant

$$(19) \quad N_0 = \frac{N}{Q} \quad (*),$$

and is to be measured in mole^{-1} , i.e. in reciprocal units for quantity of substance (**). In this representation the physical molecular weight M_{ph}^* of a body, i.e. the relative mass of one of its molecules in the physical scale of atomic weights, is defined over the molar mass M of equation (17), e.g. measured in g/mole , by the relation

$$(20) \quad M_{\text{ph}}^* = \frac{16 \times \text{molar mass of the body}}{\text{molar mass of atomic oxygen isotope } ^{16}\text{O}};$$

thus it remains as *relative* mass a dimensionless quantity. Molecular weights of elements are usually called atomic weights, A_{ph}^* , and especially for the different isotopes of an element isotopic weights, ${}_s I^*$. The oxygen isotope ^{16}O has per definitionem the isotopic weight

$$(21) \quad I^*(^{16}\text{O}) = 16.$$

The molar mass of atomic oxygen isotope ^{16}O is according to the definition of the quantity of substance unit mole

$$(22) \quad M(^{16}\text{O}) = \frac{16 \text{ g}}{1 \text{ mole}} = 16 \text{ g/mole},$$

the molar mass of an arbitrary chosen body can, in connection with equation (20), be written

$$(23) \quad M = M_{\text{ph}}^* \frac{M(^{16}\text{O})}{16} = M_{\text{ph}}^* \text{ g/mole}.$$

For the mass of a molecule μ follows from equations (1), (17) and (19)

$$(24) \quad \mu = \frac{m}{N} = \frac{MQ}{N_0 Q} = \frac{M}{N_0},$$

(*) Applying (19) to the N_0 -determination by the XRCD method one deduces, in analogy to equation (1'), the relationship

$$(19') \quad N_0 = \frac{f}{v/V},$$

V being the molar volume of the crystal under consideration.

(**) In the nomenclature used in Sect. 2, according to the above given definition of the mole, this is identical with the mole_{ph} .

i.e. Avogadro's constant is also the proportionality factor between molar mass and molecule mass of a body.

Table IV gives a survey on specific physical quantities related to mass, volume, and quantity of substance as well as on their connection with Avogadro's and Loschmidt's constants.

TABLE IV. — *Quantities describing a body which contains N equal molecules of mass μ .*

(I) General physical quantities		
mass m	volume v	quantity of substance Q
(II) Specific physical quantities		
related to mass:	related to volume:	related to quantity of substance:
specific volume v_m :	mass density ϱ :	molar mass M :
$v_m = v/m = 1/\varrho$	$\varrho = m/v = 1/v_m$	$M = m/Q = N_0 \cdot \mu$
specific molecule	molecule number	molar volume V :
number N_m :	density N_v :	$V = v/Q = N_0 \cdot \mu/\varrho$
$N_m = N/m = 1/\mu$	$N_v = N/v = \varrho/\mu$	
(III) Constants		
general physical constant, referring to quantity of substance, Q :	constant of perfect gas, referring to its volume at S.T.P., v_0 :	
Avogadro's constant N_0 :	Loschmidt's constant L_0 :	
$N_0 = N/Q = N_m \cdot M = N_v \cdot V$	$L_0 = N/v_0 = N_0/V_0$	

4. — Chemical and physical scale of atomic weights.

By definition (20) the physical molecular weight M_{ph}^* and, consequently, the physical scale of atomic weights are connected over the molar mass M with the quantity of substance Q and the unit for this latter, the mole. On the other side, there is no doubt, that at least in chemistry the chemical molecular weight M_{ch}^* and the chemical scale of atomic weights are indispensable at present. Likewise the mass quantities g-mole of equation (2) are still suitable and customary in different fields, e.g. in phenomenological thermodynamics and heat engineering, and will possibly remain so in future.

Therefore it would be appropriate to relate the mass quantities g-mole to the chemical scale in a similar way as we already did with the quantity of substance unit mole and the physical scale (see Sect. 3). The chemical molecular weight M_{ch}^* of a body, i.e. the relative mass of its molecules in the

chemical scale of atomic weights, is usually introduced over the molecule mass by the equation

$$(25) \quad M_{\text{ch}}^* = \frac{16 \times \text{mass of a molecule of the body}}{\text{mass of natural oxygen atom } \bar{\text{O}}},$$

which is, according to equation (17), equivalent to the definition

$$(25') \quad M_{\text{ch}}^* = \frac{16 \times \text{molar mass of the body}}{\text{molar mass of natural atomic oxygen } \bar{\text{O}}}.$$

The chemical atomic weight of oxygen is per definitionem

$$(26) \quad A_{\text{ch}}^*(\bar{\text{O}}) \equiv 16.$$

As conversion factor between chemical and physical scale is defined Smythe's factor

$$(27) \quad k_A = \frac{M_{\text{ph}}^*}{M_{\text{ch}}^*},$$

which can, applied to natural oxygen $\bar{\text{O}}$, especially be written with regard to (26)

$$(27') \quad k_A = \frac{A_{\text{ph}}^*(\bar{\text{O}})}{A_{\text{ch}}^*(\bar{\text{O}})} = \frac{A_{\text{ph}}^*(\bar{\text{O}})}{16};$$

thus it requires merely the experimental determination of the physical atomic weight of oxygen $\bar{\text{O}}$ in its natural isotopic composition. $A_{\text{ph}}^*(\bar{\text{O}})$ can be determined from equation

$$(28) \quad A_{\text{ph}}^*(\bar{\text{O}}) = \sum c_{\nu} I_{\nu}^*$$

with

$$(29) \quad \sum c_{\nu} = 1$$

(c_{ν} : relative abundances of ^{16}O , ^{17}O , ^{18}O ; I_{ν}^* : isotopic weights of ^{16}O , ^{17}O , ^{18}O).

The relative abundances can be computed from the concentration ratios $c(^{16}\text{O}^{17}\text{O})/c(^{16}\text{O}^{16}\text{O})$ and $c(^{16}\text{O}^{18}\text{O})/c(^{16}\text{O}^{16}\text{O})$ measured mass spectroscopically for several times. In Table V are given as examples the relative abundances c_{ν} derived from the results of THODE [29] and NIER [30] and the isotopic weights I_{ν}^* determined by SCOLMAN, QUISENBERRY and NIER [31] from mass spectroscopic measurements too. The values computed hence for $A_{\text{ph}}^*(\bar{\text{O}})$ and

k_A according to equations (28) and (27') as well as their means are listed in Table VI.

TABLE V. — Relative abundance c_v and isotopic weight I_v^* of the stable oxygen isotopes after THODE and NIER.

	Relative abundance c_v in %		Isotopic weight I_v^*
	THODE [29]	NIER [30]	
^{16}O	99.7575 ± 0.0010	99.7587 ± 0.0003	16 ± 0
^{17}O	0.0392 ± 0.0008	0.0374 ± 0.0003	17.0045364 ± 0.0000005
^{18}O	0.133 ± 0.0006	0.2039 ± 0.0002	18.0048843 ± 0.0000008

TABLE VI. — Atomic weight of « natural » oxygen in the physical scale $A_{\text{ph}}^*(\bar{\text{O}})$ and Smythe's factor k_A after THODE and NIER.

Author	Year	$A_{\text{ph}}^*(\bar{\text{O}})$	k_A	Weight p
THODE [29] . . .	1944/47	$16.00447_0 \pm 0.00009$	$1.000279_4 \pm 0.000006$	1
NIER [30]. . . .	1950	$16.00446_4 \pm 0.00003$	$1.000279_0 \pm 0.000002$	3
Mean value:		$16.00446_5 \pm 0.00005$	$1.000279_1 \pm 0.000003$	—
$A_{\text{ph}}^*(\bar{\text{O}}) = \sum c_v I_v^* \quad \sum c_v = 1$ <p style="text-align: center;">(v: ^{16}O, ^{17}O, ^{18}O)</p>				

The errors stated for mass spectroscopic data represent in general only the variability of the observed values. Especially they do not include possible variations of the « natural » relative abundances of isotopes.

We can estimate their influence at the example of oxygen; we assume a displacement of the abundance ratio $c(^{18}\text{O})/c(^{16}\text{O}) = c_{18}/c_{16}$ by $\delta(c_{18}/c_{16})/c_{18}/c_{16} = = x\%$ with c_{17} remaining constant, that being justified because $c_{17}/c_{16} \ll 1$. Under these conditions results from equations (28) and (29) for the variation of $A_{\text{ph}}^*(\bar{\text{O}})$

$$(28a) \quad \delta A_{\text{ph}}^*(\bar{\text{O}}) = \delta c_{18} (I_{18}^* - I_{16}^*)$$

with

$$(29a) \quad \delta c_{16} + \delta c_{18} = 0$$

or, as $c_{18} \ll c_{16}$ and therefore $\delta(c_{18}/c_{16}) \sim \delta c_{18}/c_{16}$,

$$(29b) \quad \delta A_{ph}^*(\bar{O}) \sim 10^{-2} x (I_{18}^* - I_{16}^*) c_{18},$$

and with equation (27'), having inserted the numerical values of Table V, for the here interesting variation of Smythe's factor

$$(27a) \quad \delta k_A = \frac{\delta A_{ph}^*(\bar{O})}{16} \approx 2.5 \cdot 10^{-5} x.$$

A variation of the abundance ratio $c(^{18}\text{O})/c(^{16}\text{O})$ by $\pm 4\%$ causes already a variation of the conversion factor k_A by $\pm 1 \cdot 10^{-5}$.

The relative abundances determined by NIER [30] (Table V) apply to oxygen of atmospheric or limestone origin. Detailed investigations, experimentally based on density determinations or mass spectroscopic measurements, showed that the abundance ratio $c(^{18}\text{O})/c(^{16}\text{O})$ may vary by several percent depending on the origin of the oxygen, e.g. $c(^{18}\text{O})/c(^{16}\text{O})$ has been found by nearly 4% higher for limestone oxygen than for oxygen from fresh water or iron ores [32-35]. To this difference of 4% corresponds a diminishing of Smythe's factor from 1.000279 to 1.000269, i.e. a relative decrease of k_A by $1 \cdot 10^{-5}$. The abundance ratio $c(^{18}\text{O})/c(^{16}\text{O})$ varies in ocean water and fresh water only by some % to 1% [35-37], whereas there have been observed variations from 1 to 5% in water from thermal decomposition products of plant leaves [34]. Also with silicate minerals and rocks of different age and origin one has found relative differences in the ratio $c(^{18}\text{O})/c(^{16}\text{O})$ up to 4% [38].

Consequently, the atomic weight of «natural» oxygen and therefore according to equation (26) the basis of the chemical scale of atomic weights are uncertain by at least $10^{-2} \%$, merely considering the occurring variation of the abundance ratio of the isotopes ^{18}O and ^{16}O . As such variations of the relative isotope abundances are experimentally not only known for oxygen or only for the lighter elements but also for elements of higher nuclear charge number, the uncertainty of chemical atomic weights caused by different origin of the elements considered can amount to some $10^{-2} \%$; i.e. on principle it becomes doubtful to strive for uncertainties smaller than $10^{-2} \%$ by precision measurements, in which enter atomic weights of the chemical scale [13, 42].

Therefore we can confine our attention to the examples for the abundance ratios of oxygen isotopes listed in Tables V and VI. Neither can a further increase in mass spectroscopic accuracy be of any advantage for Smythe's factor. The error of 0.003% , estimated for the mean value of k_A in Table VI, is already less important in view of the basic uncertainty of the chemical scale of atomic weights, which exceeds the error in k_A by one power of ten.

Occasionally it has been proposed [39] to choose as standard atom for

atomic weight scales instead of oxygen an atom with only *one* stable isotope, e.g. fluorine; the chemical atomic weight of fluorine, derived from the mass spectroscopically measured [31] isotopic weight $I_{\text{ph}}^*(^{19}\text{F})$, amounts to 18.99915, being very near to the integer 19. Adopting the proposal $A_{\text{ch}}^*(\text{F}) = A_{\text{ph}}^*(^{19}\text{F}) - 19$ would change the chemical atomic weights only by a negligible amount, whereas the physical atomic weights would be reduced nearly by Smythe's factor. Therefore it seems improbable that even to-day this idea can be realized. Furthermore, fluorine does not seem appropriate as standard atom for mass spectroscopy, as its high chemical reactivity would cause considerable corrosions at delicate parts of the apparatus.

In order to attain the best possible uniform conversion between both scales, it would be desirable to agree on a conventional value for k_A between 1.000 27 and 1.000 28. The Commission on Atomic Weights of the International Union of Pure and Applied Chemistry has discussed the value 1.000275 [40]. Considering the data observed with atmospheric and limestone oxygen a higher value seems to be preferable. Here is used in Sect. 2 and 5 the mean of Table VI

$$(30) \quad k_A = 1.000\,279 \pm 0.000\,003.$$

On the other hand it should not be disregarded that in the physical scale of atomic weights up to now the isotopic weights are still not known for all elements with the desirable accuracy; the same holds for the relative abundances of the stable isotopes of some elements. Until these gaps will be filled by further development of mass spectroscopy and nuclear reaction data, it will be necessary to revert also in atomic physics in special cases to the chemical atomic weights.

It is for the above explained reasons that one should endeavour to distinguish clearly the quantities and units based on the chemical scale from those connected with the physical scale. To the chemical scale of molecular weights M_{ch}^* should suitably be related the specific molecule number, N_m of equation (1), the specific volume of perfect gas at S.T.P., v_{m_0} of equation (7), and related quantities; especially should be restricted to it the mass quantities grammole:

$$(31) \quad \text{g-mole} \equiv \text{g-mole}_{\text{ch}} \equiv M_{\text{ch}}^* \text{ g}.$$

However the quantity of substance, Q , and its basic unit mole should only be connected with the physical scale of molecular weights M_{ph}^*

$$(32) \quad \text{mole} \equiv \text{mole}_{\text{ph}}$$

as well as Avogadro's constant, N_0 of equation (19), the molar mass, M of equation (17), the molar volume, V of equation (18), and related quantities.

TABLE VII. — *Quantities and units connected with atomic weight scales.*

(I) Connected with the physical scale of atomic weights

mole: basic unit for quantity of substance, Q ,

primary standard: oxygen isotope ^{16}O

relative molar mass: physical molecular weight M_{ph}^* ,

$$M_{\text{ph}}^* = \frac{16 \times \text{molar mass of body } X}{\text{molar mass of atomic oxygen isotope } ^{16}\text{O}} = 16 \frac{M(X)}{M(^{16}\text{O})}.$$

Avogadro's constant: $N_0 = N/Q = n_0 \text{ mole}^{-1}$ ($n_0 \approx 6.025 \cdot 10^{23}$)

mass unit in mass spectroscopy: defined as mass of an atom, μ_1 ,
of a monisotopic element with $A_{\text{ph}}^* \equiv 1$,

$$1 \text{ MU} = \mu_1 = \frac{1}{n_0} \text{ g}.$$

(II) Connected with the chemical scale of atomic weights

relative mass: chemical molecular weight M_{ch}^*

$$M_{\text{ch}}^* = \frac{16 \times \text{mass of a molecule of body } X}{\text{mass of natural atomic oxygen } \overline{\text{O}}} = 16 \frac{\mu(X)}{\mu(\overline{\text{O}})},$$

grammole: characteristic of any particular substance, defined as M_{ch}^* gram,

$$1 \text{ g-mole} = M_{\text{ch}}^* \text{ g}.$$

The handicap, however, remains that both, the g-mole of equation (31) and the mole of equation (32), which differ in many respects, have similar names — therefore, in case the use of the grammole will continue in future, it would be desirable to find a new name for it [42].

Another mass unit linked to the *physical* scale of atomic weights is the *atomic mass unit* with the symbolic abbreviation MU, which is now generally used to measure and state the mass of atoms, especially their isotopes, in atomic and nuclear physics. It is defined as the mass of a hypothetical atom of the physical atomic weight $A_{\text{ph}}^* \equiv 1$. According to equations (24), (9), and (23) the mass of an atom, μ , can be represented as

$$(24') \quad \mu = \frac{M}{N_0} = \frac{M}{n_0} \text{ mole} = \frac{A_{\text{ph}}^*}{n_0} \text{ g},$$

leading for the mass unit (*) to

$$(33) \quad 1 \text{ MU} = \frac{1}{n_0} \text{ g}.$$

(*) Another mass unit, called «dalton», is connected with the *chemical* scale of atomic weights and defined, in analogy to MU, as the mass of a hypothetical atom of the

Avogadro's constant N_0 appears as proportionality factor between molecule number and quantity of substance or between molar mass and molecule mass of a body, whereas Avogadro's number n_0 is the conversion factor between the units g and MU.

Table VII gives a survey on quantities and units connected with the physical and the chemical scale of atomic weights.

5. - Loschmidt's constant, molar volume of a perfect gas at S.T.P., gas constant, Boltzmann's entropy constant.

According to its definition *Loschmidt's constant* does not depend on the one or the other interpretation of the «mole». It is defined with the conception of molecule number density as quotient from the specific molecule number and the specific standard volume of a perfect gas

$$(7) \quad L_0 = \frac{N_m}{v_{m_0}},$$

and with the conception of quantity of substance as quotient from Avogadro's constant and molar volume of a perfect gas at standard conditions

$$(34) \quad L_0 = \frac{N_0}{V_0},$$

v_{m_0} and V_0 being related to standard temperature and pressure (41/42).

With equations (17) and (18) the molar volume V can be expressed by the density ϱ and the molar mass M

$$(18') \quad V = \frac{v}{\varrho} = \frac{v}{m} \frac{m}{\varrho} = \frac{M}{\varrho},$$

chemical atomic weight $A_{\text{ch}}^* = 1$. According to equations (1), (4), and (2) the mass of an atom, μ , can be also written

$$\mu = \frac{1}{N_m} = \frac{1}{n_m} \text{ g-mole} = \frac{A_{\text{ch}}^*}{n_m} \text{ g},$$

leading for the dalton to

$$1 \text{ dalton} = \frac{1}{n_m} \text{ g}.$$

Hence n_m , the numerical value of the specific molecule number in g-mole⁻¹ of equation (31), is the conversion factor between the units g and dalton.

and linked to the physical molecular weight M_{ph}^* using the relation (23)

$$(18'') \quad V = \frac{M_{ph}^*}{\rho} \frac{g}{\text{mole}}.$$

Thus, to determine V_0 , it is only necessary to know the molecular weight M_{ph}^* and the standard density ρ_0 of an ideal gas or a real gas correcting for its deviation from the ideal state.

In general one chooses molecular oxygen — on one side, because the standard density of the real gas and the reduction factor to the ideal state are reliably known for oxygen, on the other hand, because its molecular weight in the chemical scale amounts per definitionem to 32 [42]. As, however, for the evaluation of the molar standard volume according to equation (18'') the physical and not the chemical molecular weight is required, Smythe's factor k_A enters also into the calculation. This goes back to the fact, that up to now precision measurements for the density of isotopically pure oxygen, i.e. of $^{16}\text{O}^{16}\text{O}$ -molecules, are not yet made. Involving Smythe's factor can also not be avoided if one starts from the definition (7) for Loschmidt's constant using the specific molecule number N_m , which is related to the chemical scale of atomic weights and measured in g-mole^{-1} of equation (31) — the conversion factor k_A would only change his place and reappear with the determination of the N_m -value.

As long as precise density determinations with $^{16}\text{O}^{16}\text{O}$ cannot be established, the precision attainable for L_0 is limited by the basic uncertainty in the definition or realization of the chemical scale of atomic weights; according to the discussion in Sect. 4 it is up to now not possible to reduce the relative uncertainty more than to one or several 10^{-5} . The still uncertain knowledge of Avogadro's constant is a further handicap of the same order of magnitude.

With the standard density of the perfect gas, evaluated with oxygen [42],

$$(35) \quad \rho_0 = (1.427\,647 \pm 0.000\,04) \cdot 10^{-3} \text{ g/cm}^3,$$

and

$$(26') \quad M_{ch}^*(\bar{\text{O}}) \equiv 32$$

$$(30) \quad k_A = 1.000\,279 \pm 0.000\,03$$

$$(15c) \quad N_0 = 6.025\,0 \cdot 10^{23} \text{ mole}^{-1}$$

one obtains for Loschmidt's constant a value which is near to

$$(36) \quad L_0 = 2.687\,24 \cdot 10^{19} \text{ cm}^{-3}$$

and differs from the true value of L_0 probably only by several $10^{-2} \%$.

The *molar volume of a perfect gas at S.T.P.*, related to the *physical scale*, is according to equation (18'')

$$(37) \quad V_0 = \frac{k_A M_{\text{ch}}^*}{\rho_0} \frac{\text{g}}{\text{mole}} = (2.242\,08 \pm 0.000\,06) \cdot 10^4 \text{ cm}^3/\text{mole},$$

the *specific standard volume of a perfect gas*, related to the *chemical scale*,

$$(38) \quad v_{m0} = \frac{1}{\rho_0} = (2.241\,45 \pm 0.000\,06) \cdot 10^4 \text{ cm}^3/\text{g-mole}.$$

Finally, two important constants of thermodynamics, kinetics, and statistics shall be mentioned:

gas constant

$$(39) \quad R_0 = \frac{p_0 V_0}{T_0},$$

and *Boltzmann's entropy constant*

$$(40) \quad k = \frac{R_0}{N_0}.$$

In physics one has adopted as standard conditions: standard pressure p_0 and ice point T_0 ; their values have been fixed by the 9th and 10th General Conference of Weights and Measures [41]:

$$(41) \quad p_0 = 1 \text{ atm} = 1\,013\,250 \text{ dyn/cm}^2$$

$$(42) \quad T_0 = 273.15 \text{ }^\circ\text{K}.$$

With the values (37) and (15c) for V_0 and N_0 one obtains

$$(39') \quad R_0 = (8.316\,9_s \pm 0.000\,3) \cdot 10^7 \text{ erg/}^\circ\text{K mole}$$

$$(40') \quad k = 1.380\,4_1 \cdot 10^{16} \text{ erg/}^\circ\text{K}.$$

The last value calculated with N_0 will probably not differ from the true value of Boltzmann's constant by more than several $10^{-2} \text{ }_{\text{‰}}$.

6. - Conclusions.

Questions of nomenclature regarding the terms « constant » and « number » in connection with the names AVOGADRO and LOSCHMIDT are cleared up cor-

responding to the definition and meaning of both constants. The numerical values for Avogadro's constant N_0 , published during the last 10 years, result from (1) *direct experimental determination* by the X-ray-crystal-density method and, (2) *least-squares adjustment* of the observational data from precision measurements of atomic constants. The N_0 -values determined according to (1) or (2) differ from each other by at least some $10^{-2}\%$ irrespective whether they refer to the chemical or to the physical scale of atomic weights. This statement holds also for $N'_0 = k_\lambda^3 \cdot N_0$, the values nowadays recommended for the conversion factor $k_\lambda = 10^{21}$ XU/cm being partly by $2 \cdot 10^{-5}$ higher than the value 1.00202 adopted in 1947. Therefore, so far N_0 does not seem appropriate as basic constant for general definitions. From the discussion results that the true value for N_0 will be near to $6.0250 \cdot 10^{23}$ mole $^{-1}$ (physical scale) and will probably not differ from this value by more than several $10^{-2}\%$. There may contribute to clear up and to eliminate the discrepancies still existing: (1) new direct experimental N_0 -determinations by the XRCD method, measuring all parameters at the same sample, determining the degree of lattice-imperfections by further investigations, and evaluating k_λ anew; (2) least-squares adjustment using new experimental results from further precision measurements of atomic constants as soon as they will be established; in this case it would as well be desirable to determine new N_0 -values by the XRCD method. «Siegbahn's» Avogadro's constant $N'_s = 6.0594 \cdot 10^{23}$ mole $^{-1}$ (chemical scale) is only suitable for special cases, e.g. in crystallography.

These facts are rather important for the definition of the «mole». Up to now, in the continuum-theoretical description of macrophysics, individual mass quantities have been meant by the grammole, i.e. the mass $M^* \text{ g}$ ($A^* \text{ g}$ respectively), whose amount varies from substance to substance according to its molecular weight M^* (atomic weight A^* respectively). To the atomistic conception corresponds the definition of the mole as unit of the basic physical quantity «quantity of substance» Q , which is proportional to the number N of molecules in a body, the proportionality factor being Avogadro's constant $N_0 = N/Q = M/\mu$ (M = molar mass, μ = mass of molecule). Defining the mole, unit for quantity of substance, as the quantity of substance of a body with n_0 molecules (n_0 = Avogadro's number, i.e. the numerical value of N_0 in mole $^{-1}$) would not be efficient because of the still existing uncertainty for n_0 . On the other side, the definition «1 mole is the quantity of substance of a body containing as many equal individuals (molecules, atoms, ions, radicals etc.) as atoms are contained in exactly 16 g oxygen isotope ^{16}O » offers the advantage to be directly linked to precision methods of mass spectroscopy and is independent of the knowledge of Avogadro's number, which now appears as conversion factor between the atomic mass unit (MU) and the gram (g): $1 \text{ g} = n_0 \text{ MU}$.

For application of the physical mole in chemistry one must know the con-

version factor $k_A = A_{\text{ph}}^*/A_{\text{ch}}^*$ between chemical and physical scale of atomic weights, which can be determined with a given sample of atmospheric oxygen within a few 10^{-3} ‰ : $k_A = 1.000\,279$. However, the variations observed for the abundance ratios of the stable isotopes of elements (especially of oxygen as standard atom of atomic weight scales) cause for k_A an uncertainty of some 10^{-2} ‰ , which cannot be reduced, and lead, at the same extent, to a basic impossibility of fixing the chemical scale unambiguously. It is also for this reason, that oxygen isotope ^{16}O is recommended as primary standard for the mole, i.e. that the mole as unit of quantity of substance should be related to the physical scale; on the other side, it would be suitable to define the gram-mole up to now customary by the chemical molecular weights.

With the molar volume of a perfect gas at S.T.P.,

$$V_0 = (2.242\,08 \pm 0.000\,06) \cdot 10^4 \text{ cm}^3 \text{ mole}^{-1} \quad (\text{physical scale}),$$

and the gas constant,

$$R_0 = (8.316\,9_8 \pm 0.000\,3) \cdot 10^7 \text{ erg } ^\circ\text{K}^{-1} \text{ mole}^{-1} \quad (\text{physical scale}),$$

one obtains for Loschmidt's constant $L_0 = N_0/V_0$ and for Boltzmann's entropy constant $k = R_0/N_0$ the values $2.687\,2_4 \cdot 10^{19} \text{ cm}^3$ and $1.380\,4_1 \cdot 10^{-16} \text{ erg } ^\circ\text{K}^{-1}$ respectively, which can differ from the true values of L_0 and k by several 10^{-2} ‰ .

REFERENCES

- [1] A. AVOGADRO: *Journ. Phys. Chim.*, **73**, 58 (1811).
- [2] W. OSTWALD: *Ostwalds Klassiker der exakten Naturwissenschaften*, No. 8, *Die Grundlagen der Molekulartheorie* (Leipzig, 1889), note 3, p. 48.
- [3] J. LOSCHMIDT: *Sitzungsber. kaisl. Akad. Wiss. Wien*, **52**, 395 (1865), Abt. II.
- [4] R. CLAUSIUS: *Phil. Mag.*, (2) **19**, 434 (1836).
- [5] S. E. VIRGO: *Sci. Progr.*, **27**, 634 (1932-33).
- [6] W. L. BRAGG: *Journ. Sci. Instr.*, **24**, 27 (1947); E. A. WOOD: *Phys. Rev.*, (2) **72**, 436 (1947).
- [7] COMITÉ INTERNATIONAL DES POIDS ET MESURES: *Proc. Verb. Com. Internat. Poids Mes.*, (2) **22**, 77 (1950).
- [8] R. T. BIRGE: *Amer. Journ. Phys.*, **13**, 63 (1945).
- [9] U. STILLE: *Zeits. f. Phys.*, **125**, 174 (1948).
- [10] M. E. STRAUMANIS: *Zeits. f. Phys.*, **126**, 49, 65 (1949); *Acta Cryst.*, **2**, 82 (1949); *Journ. Appl. Phys.*, **20**, 726 (1949).
- [11] F. KIRCHNER: in LANDOLT-BÖRNSTEIN, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik*, (Berlin-Göttingen-Heidelberg, 1950), Sect. 12, p. 30.
- [12] N. W. H. ADDINK: *Rec. Trav. Chim.*, **70**, 202 (1951).

- [13] U. STILLE: *Phys. Bl.*, **8**, 397 (1952).
- [14] M. E. STRAUMANIS: *Phys. Rev.*, (2) **92**, 1155 (1953).
- [15] M. E. STRAUMANIS: *Phys. Rev.*, (2) **95**, 566 (1954).
- [16] G. BROGREN: *Ark. f. Fys.*, **7**, 47 (1954).
- [17] A. SMAKULA, J. KALNAJS and V. SILS: *Phys. Rev.*, (2) **99**, 1747 (1955).
- [18] E. R. COHEN and J. W. M. DU MOND: *Phys. Rev.*, (2) **98**, 1128 (1955).
- [19] M. SIEGBRAH: *Spektroskopie der Röntgenstrahlen*. 2nd ed. (Berlin, 1931). p. 43.
- [20] J. W. M. DU MOND and E. R. COHEN: *Rev. Mod. Phys.*, **20**, 82 (1948); **21**, 651 (1949).
- [21] J. A. BEARDEN, F. T. JOHNSON and H. M. WATTS: *Report of July 31, 1950*, Contract Nord 8036; J. A. BEARDEN and H. M. WATTS: *Phys. Rev.*, (2) **81**, 73 (1951).
- [22] J. W. M. DU MOND and E. R. COHEN: *Report of December 1950*, ONR Contract N6-onr-244, Task 4; *Phys. Rev.*, (2) **82**, 555 (1951).
- [23] E. E. WITMER: *Phys. Rev.*, (2) **81**, 308 (1951).
- [24] J. W. M. DU MOND and E. R. COHEN: *Amer. Sci.*, **40**, 447 (1952).
- [25] J. W. M. DU MOND and E. R. COHEN: *Rev. Mod. Phys.*, **25**, 691 (1953); *Phys. Rev.*, (2) **94**, 1790 (1954).
- [26] J. A. BEARDEN and J. S. THOMSEN: *A survey of atomic constants*, Contract Nord 11299, (Baltimore, 1955).
- [27] E. R. COHEN, J. W. M. DU MOND, TH. W. LAYTON and J. S. ROLLET: *Rev. Mod. Phys.*, **27**, 363 (1955).
- [28] W. H. WESTPHAL: *Phys. Bl.*, **10**, 404 (1954).
- [29] H. G. THODE: *Nat. Res. Council, McMaster Univ. Hamilton, Ontario*, Report No. MC-57, April 29, 1944; K. T. BAINBRIDGE: *Abstr. Proc. 7. Solvay Congr.* (Brussels, Sept. 22-27, 1947).
- [30] A. O. NIER: *Phys. Rev.*, (2) **77**, 789 (1950).
- [31] T. T. SCOLMAN, K. S. QUISENBERRY and A. O. NIER: *Phys. Rev.* (2) **102**, 1076 (1956).
- [32] M. DOLE: *Journ. Amer. Chem. Soc.*, **57**, 2731 (1935); M. DOLE and R. L. SLOBOD: *Journ. Amer. Chem. Soc.*, **62**, 471 (1940); M. DOLE, G. A. LANE, D. P. RUDD and D. A. ZAUKELES: *Geochim. Cosmochim. Act.*, **6**, 65 (1954).
- [33] H. G. THODE: *Research*, **2**, 154 (1949).
- [34] R. H. VROOMAN: *M. Sc. Thesis*, 1948; McMaster University, Canada.
- [35] C. H. GREENE and R. J. VOSKUYL: *Journ. Amer. Chem. Soc.*, **58**, 693 (1936); **61**, 1342 (1939).
- [36] S. EPSTEIN and T. MAYEDA: *Geochim. Cosmochim. Act.*, **4**, 213 (1953).
- [37] W. DANSGAARD: *Geochim. Cosmochim. Act.*, **6**, 241 (1954).
- [38] H. SCHWANDER: *Geochim. Cosmochim. Act.*, **4**, 261 (1953); P. BAERTSCHI and R. S. SILVERMAN: *Geochim. Cosmochim. Act.*, **1**, 317 (1951); R. S. SILVERMAN: *Geochim. Cosmochim. Act.*, **2**, 26 (1952).
- [39] *Symposium für Präzisionsbestimmung von Atomkernmassen im Max-Planck-Institut für Chemie* (Mainz, July 10-12, 1956); V. CAGLIOTI: «Il problema della scala doppia dei pesi atomici ...» in this issue.
- [40] UNION INTERNATIONALE DE CHIMIE PURE ET APPLIQUÉE: *Compt. Rend. 17^e Conf. U.I.C.P.A.* (Stockholm, 1953), p. 39; *Compt. Rend. 18^e Conf. U.I.C.P.A.* (Zürich, 1955), p. 115; V. CAGLIOTI: «Il problema della scala doppia dei pesi atomici ...» in this issue.
- [41] CONFÉRENCE GÉNÉRALE DES POIDS ET MESURES: *Compt. Rend. 9^e Conf. gén. Poids Mes.* (Paris, 1948 [1949]), p. 55; *Compt. Rend. 10^e Conf. gén. Poids Mes.* (Paris, 1954 [1955]), p. 79.
- [42] U. STILLE: *Messen und Rechnen in der Physik* (Braunschweig, 1955), p. 117 ff., 125 ff., 190 ff., 322 ff.

A New Determination of Avogadro's Number from Lattice Constant and Density of Single Crystals (*).

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Avogadro's number (**), defined as the number of molecules per mole, plays an important role as one of the fundamental physical constants. It is desirable to know the value of this constant quite accurately in order to derive others with the required accuracy. Although there are over 20 methods [1] for the determination of Avogadro's number, the published values vary in the third decimal place even for the same method and material. The uncertainty of data computed by the method of least squares is of the same order [2].

In this paper, we shall discuss only the determination of Avogadro's number from the lattice constants and density of crystals.

Avogadro's number N is connected with other crystal constants by $N = nM/\varphi \rho a^3$, where n is the number of molecules in the unit cell; M , the molecular weight; φ , a geometrical factor, which for cubic crystals is unity; ρ , the density in g/cm^3 and a , the lattice constant in cm.

This method has been used already by BIRGE [3], STRAUMANIS [4] and BROGREN [5] (Table I). Only calcite was used by all three authors, but each one obtained a different result. The difference in calcite is even greater than between other crystals.

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(**) From the historical point of view, AVOGADRO stated, in 1811, the famous hypothesis that at the same pressure and temperature equal volumes of gases contain equal numbers of molecules. In 1865 LOSCHMIDT made a first actual computation of the number of molecules per cm^3 . Therefore, in European literature Avogadro's number is called Loschmidt number.

TABLE I. — *Avogadro's number computed from lattice constants and densities (chemical scale) (*)*.

Crystal	N (chemical scale)	Author
Calcite	$(6.023\,14 \pm 0.000\,39) \cdot 10^{23} \text{ mole}^{-1}$	BIRGE
»	$(6.023\,27 \pm 0.000\,17) \cdot 10^{23} \text{ »}$	BROGREN
»	$(6.024\,03 \pm 0.000\,30) \cdot 10^{23} \text{ »}$	STRAUMANIS
Diamond	$(6.023\,43 \pm 0.000\,59) \cdot 10^{23} \text{ »}$	BIRGE
KCl	$(6.023\,24 \pm 0.000\,52) \cdot 10^{23} \text{ »}$	BIRGE
LiF	$(6.023\,19 \pm 0.000\,80) \cdot 10^{23} \text{ »}$	BIRGE
NaCl	$(6.024\,01 \pm 0.000\,52) \cdot 10^{23} \text{ »}$	BIRGE
Quartz	$(6.023\,72 \pm 0.000\,18) \cdot 10^{23} \text{ »}$	BROGREN

(*) The following conversion factors were used:

λ_g/λ_s	$A_{\text{phys}}/A_{\text{chem}}$	Author
1.002 03	1.000 272	BIRGE
1.002 02	1.000 272	BROGREN
1.002 02	1.000 272	STRAUMANIS

The values computed by the method of least squares on the basis of the consistency of the fundamental constants vary also from year to year, as one can see from the DuMOND and COHEN data in Table II.

TABLE II. — *Computed Avogadro's numbers (chemical scale)*.

Author	Year	$N \cdot 10^{-23}$ (mole ⁻¹)
DuMOND and COHEN [6]	1950	$6.023\,76 \pm 0.000\,11$
BEARDEN and WATTS [7]	1951	$6.024\,02 \pm 0.000\,17$
STILLE [8]	1952	$6.023\,65 \pm 0.000\,15$
DuMOND and COHEN [9]	1953	$6.023\,04 \pm 0.000\,36$
DuMOND and COHEN [2]	1955	$6.023\,18 \pm 0.000\,16$

Although the given uncertainties of individual computations vary only between 1.1 and $3.6 \cdot 10^{-4}$, the difference between the values is between 1.4 and $9.8 \cdot 10^{-4}$.

1. — Discussion of errors.

The errors are caused by uncertainties in atomic weights, lattice constants and densities, and by material defects. The atomic weights are under the control of the International Commission on Atomic Weights. The data are published every second year with some changes, but the accuracy is not given.

These data are given, for the most part, only to the second decimal place. The mass-spectroscopic measurements give atomic weights at least to the third decimal place. In Table III are listed the International and mass-spectroscopic atomic weights for eight crystals that are of interest here. Germanium shows a striking difference between the International and mass-spectroscopic atomic weights, indicating that its atomic weight is incorrect by 0.03. As we see from the last column in Table III, the error of the International atomic weights is from $4 \cdot 10^{-7}$ to $40 \cdot 10^{-5}$ [10].

TABLE III. - *International and mass-spectroscopic atomic and molecular weights.*

	A_i	$A_{m.s.}$	ΔA	$\Delta A/A$
Al	26.98	26.98256	0.00256	$9.5 \cdot 10^{-5}$
CaF	78.08	78.079	0.001	$1.3 \cdot 10^{-5}$
Ge	72.60	72.630	0.030	$41.6 \cdot 10^{-5}$
Si	28.09	28.0875	0.0025	$8.9 \cdot 10^{-5}$
CsI	259.82	259.821	0.0001	$3.8 \cdot 10^{-7}$
SiO ₂	60.09	60.0875	0.0025	$4.2 \cdot 10^{-5}$
TlCl	239.847	239.852	0.005	$2.1 \cdot 10^{-5}$
TlBr	284.306	284.301	0.005	$1.8 \cdot 10^{-5}$

Using mass-spectroscopic atomic weights, we obtain Avogadro's number on the physical scale. For conversion into the chemical scale, we have to use one of the three conversion factors:

1.000272 \pm 0.000005	BIRGE 1941 [11]
1.0002783	NIER 1950 [12]
1.000275	Intern. Comm. 1954 [13]

Although the difference between the three values is only in the sixth decimal place, it causes a difference in N of 2 to 4 units in the fifth place.

2. - Lattice-constants error.

A series of errors influence the accuracy of the lattice constant measurements. From the equation for cubic crystals, $a = (\lambda/2)\sqrt{h^2 + k^2 + l^2}/\sin \theta$, the lattice constant is determined by λ and θ . The λ error, according to BRAGG [14] consists of $\pm 0.001\%$ error in the original kX-units and $\pm 0.003\%$ for the conversion factor λ_g/λ_s , or a total of $\pm 0.004\%$. From crystallographic and grating X-ray measurements $\lambda_g/\lambda_s = 1.002020$. Since $\text{CuK}_{\alpha_1}\lambda$ has been changed from 1.54050 to 1.54051 Å [15], we have $\lambda_g/\lambda_s = 1.002026$. However, the newest universal value according to DuMond and Cohen [2] is

$\lambda_a/\lambda_s = 1.002\,039 \pm 0.000\,014$. If we assume the error obtained for the universal value, then λ is uncertain by 0.003% or, for CuK_{α_1} , $4.6 \cdot 10^{-5} \text{ \AA}$.

3. - The diffraction angle error.

The influence of the diffraction angle θ is given by $\Delta a/a = -(\cot \theta) \Delta \theta$. Assuming $\Delta \theta = 0.002^\circ$ and $\theta = 80^\circ$, $\Delta a/a = 0.0006\%$. This is approximately the limit that can be achieved with the best modern instruments under very favorable conditions.

4. - Material error.

All materials contain imperfections caused partly by impurities and partly by lattice defects. The lattice constant can be raised or lowered and we can not predict what the true lattice should be. Only a comparison of a series of crystals grown under various conditions can give us information as to which lattice constant is closer to the ideal one. As an example, there is shown in Fig. 1 a change of a synthetic KBr crystal along the growing direction. Since the impurities concentrate in the melt as the growth progresses and the lattice constant decreases, we have a proof that the highest lattice in this case corresponds to the purest crystal. This method can not be applied to natural crystals because the direction of growth is not known and generally the impurity will be distributed homogeneously. In this case, other methods, e.g., conductivity, absorption, luminescence may help in the evaluation of material. How much even the best natural crystals can be contaminated by impurities can be seen from the following two examples. For rock salt from various localities, lattice constants vary [16] from 5.62895 to 5.62912 \AA , and for calcite [1] d_{100} from 3.02786 to 3.02901 \AA (data for both crystals are not corrected for refraction).

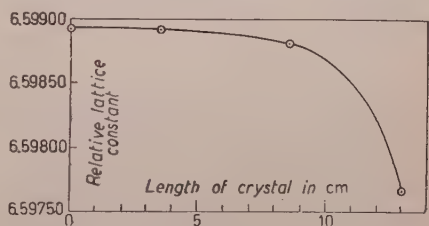


Fig. 1.

5. - Systematic errors.

The most serious errors in lattice constant determinations are the systematic errors, which are inherent in all methods. Their elimination is done either by the improvement of the methods or by corrections of the results [17].

Neither method is perfectly satisfactory. The most reliable results can be obtained by a comparison of data from the same materials by various methods. Unfortunately, this is not done at present. The agreement between various methods used on the same material but on different samples is in the fourth decimal place [18], but in only a few cases.

6. - Density error.

In density determinations the main errors are caused by errors in the density of the liquid used either for flotation or hydrostatic weighing, the temperature and the quality of the material. The standard for all density measurements is specially purified water. Close temperature control with calibrated thermometers is always necessary. Concerning the material, all precautions mentioned already in the discussion of lattice constant, have to be taken and, in addition, the crystals have to be examined for bubbles, cracks and smooth surfaces.

The density errors, as given in the literature [19], are only in a few cases between 4 to $6 \cdot 10^{-5}$; in most cases the fourth place is already uncertain.

The following Table IV summarizes the errors. The main errors are caused by density and λ . In addition the material imperfections are always present and have to be controlled.

TABLE IV. - *Main errors which influence the computation of Avogadro's number.*

$\Delta A/A$	$3(\Delta\lambda/\lambda)$	$3(\Delta a/a)$	$\Delta \rho/\rho$	Total
$2 \cdot 10^{-5}$	$9 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	$4 \cdot 10^{-5}$	$1.7 \cdot 10^{-4}$

7. - A new determination of Avogadro's number.

In connection with our study of crystal imperfections, it was necessary to have a reliable and most accurate value of Avogadro's number. We decided therefore to redetermine Avogadro's number using better material and measuring lattice constants and densities on the same samples with the greatest possible accuracy. To avoid any uncontrollable influence of material imperfections, we selected a group of crystals which differ in crystal structure, chemical bonding, lattice constant and density. In such a variety we may expect a different kind and number of defects which will not have a unidirectional influence on our measurements.

The following crystals have been used: Al, CaF_2 , CsI, Ge, Si, SiO_2 , TiCl

and TlBr. Of these crystals Si and Ge had less impurity than 0.0001%; Al, CaF_2 , TlCl and TlBr less than 0.001%; only CsI had ca. 0.01% Rb.

The density has been determined on large samples (1 to 20 cm^3) by hydrostatic weighing using ethylene bromide as the immersion liquid. The temperature was kept constant to within 0.01 $^\circ\text{C}$. All necessary corrections were applied in computation [20]. The lattice constants were determined by an X-ray Geiger-counter diffractometer. The method and errors involved were discussed in our previous paper [18].

The results are given in the following table.

TABLE V. — *New crystal data used in the computation of Avogadro's number.*

Crystal	n	A in mole	d_{25} in g/cm^3	a_{25} in \AA	$N \cdot 10^{-23}$ (mole^{-1})
Al	4	26.982 56	2.698 01	4.049 60	6.023 70
CaF_2	4	78.079	3.179 34	5.463 42	6.023 70
CsI	1	259.821	4.525 93	4.567 72	6.023 76
Ge	8	72.630	5.326 73	5.756 53	6.023 68
Si	8	28.087 5	2.329 02	5.430 72	6.023 64
SiO_2	3	60.087 5	2.648 45	a : 4.913 29 c : 5.404 83	6.023 72
TlCl	1	239.852	7.018 29	3.842 47	6.023 94
TlBr	1	284.301	7.452 92	3.985 88	6.023 92

In the computation we used: $\lambda_g/\lambda_s = 1.002\,026$ corresponding to $\text{CuK}_{\alpha_1}\lambda = 1.54051 \text{ \AA}$ and the conversion factor from physical to chemical scale: 1.0002783.

Of all our data only three are somewhat higher than the rest. The higher value of CsI is caused by Rb impurities and in TlCl and TlBr we have to assume vacancies. If we disregard these three values we obtain

$$N = (6.025\,36 \pm 0.000\,02) \cdot 10^{23} \text{ mole}^{-1} \text{ (physical scale),}$$

or

$$N = (6.023\,68 \pm 0.000\,02) \cdot 10^{23} \text{ mole}^{-1} \text{ (chemical scale).}$$

8. — Discussion.

Of all available data the value of BIRGE [3] $(6.023\,38 \pm 0.000\,23) \cdot 10^{23} \text{ mole}^{-1}$ (chemical scale) is generally considered the most reliable. It has been used by DUMOND and COHEN [2] as input value in their computation of consistent

universal physical constants by the method of least squares. BIRGE's value is based on the data on five crystals (calcite, diamond, KCl, LiF and NaCl). Of these the data on calcite and LiF are not reliable. If we eliminate these two values and use the same conversion factors as in our computations, the Birge value agrees with ours within 0.00001.

We consider therefore the above value as the most probable at present and recommend using it as the input in the computation of consistent universal physical constants by the method of least squares.

REFERENCES

- [1] S. E. VIRGO: *Sci. Progr.*, **27**, 634 (1933).
- [2] E. R. COHEN, J. W. M. DuMOND, T. W. LAYTON and J. S. ROLLETT: *Revs. Mod. Phys.*, **27**, 363 (1955).
- [3] R. T. BIRGE: *Am. Journ. Phys.*, **13**, 63 (1945).
- [4] M. E. STRAUMANIS: *Acta Cryst.*, **2**, 82 (1949).
- [5] G. BROGREN: *Ark. f. Fys.*, **7**, 47 (1953).
- [6] J. W. M. DuMOND and E. R. COHEN: ONR Contract N6-onr-244, Task 4, Cal. Inst. Tech. (1950), p. 116.
- [7] J. A. BEARDEN and H. M. WATTS: *Phys. Rev.*, **81**, 73 (1951).
- [8] U. STILLE: *Phys. Blätter*, **9**, 397 (1952).
- [9] J. W. M. DuMOND and E. R. COHEN: *Revs. Mod. Phys.*, **25**, 691 (1953).
- [10] M. E. STRAUMANIS, *Zeits. f. Phys.*, **126**, 49 (1949), assumes $5 \cdot 10^{-5}$, which is on the lower side.
- [11] R. T. BIRGE: *Rev. Mod. Phys.*, **13**, 233 (1941).
- [12] A. O. NIER: *Phys. Rev.*, **77**, 789 (1950).
- [13] E. WICHERS: *Journ. Am. Chem. Soc.*, **76**, 2033 (1954).
- [14] W. L. BRAGG: *Journ. Sci. Instr.*, **24**, 27 (1947).
- [15] K. LONSDALE: *Acta Cryst.*, **3**, 400 (1950).
- [16] M. STRAUMANIS and A. LEVINS: *Die Präzisionsbestimmungen von Gitterkonstanten nach der asymmetrischen Methode* (Berlin, 1940).
- [17] H. P. KLUG and L. E. ALEXANDER: *X-ray Diffraction Procedures* (New York, 1954).
- [18] A. SMAKULA and J. KALNAJS: *Phys. Rev.*, **99**, 1737 (1955).
- [19] D. A. HUTCHISON: *Journ. Chem. Phys.*, **13**, 383 (1945).
- [20] A. SMAKULA and V. SILS: *Phys. Rev.*, **99**, 1744 (1955).

A Note on the Determination of the Avogadro Number.

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Some thirty years ago the dimensions of the unit cell of crystals were put to the test by comparing the density of crystals found by weighing and the density calculated from the equation:

$$(1) \quad N = f \cdot M / V \cdot D,$$

where

N = the Avogadro number taken from Millikan's oil-drop measurements;

f = a factor related to the number of molecules per unit cell;

M = the molecular weight;

V = the volume of the unit cell and

D = the density of the crystal.

Afterwards, as some doubt arose about the used value of N , the same equation was applied in order to *determine* the value of N .

It was then found necessary to know the density of perfect crystals as accurately as possible. Because of the fact that D_w (the density found by weighing) was found to be less than D_r (the density as determined from X-ray data), the highest value of D for a special substance was considered to be the most accurately one.

In order to compare measurements on different substances the value of N is calculated according to formula (1), the lowest value being considered to be the «true value».

Deviations from that value are a measure for the imperfection of the crystals (lattice imperfections, vacancies, etc.).

* * *

In X-ray research on crystals, in the period from 1920 to 1930, the dimensions of the unit cell, found experimentally, were put to test by numerous workers, who compared the crystallographic density D_r calculated with

the aid of N (the Avogadro number) with D_w the value found experimentally (by weighing). D_w was usually found to be smaller than D_r . At that time the value of the Avogadro number was taken from Millikan's oil-drop measurements.

In the decade that followed, attention was strongly focussed on crystal imperfections (mosaic blocks), and the writer of this article was prompted to undertake an investigation of such faults [1].

It was necessary therefore to determine the value N as accurately as possible and afterwards its deviations, depending upon the physical and chemical habit of the crystals investigated, such as impurities, non-stoichiometric composition, macro-holes and lattice vacancies.

In the above-mentioned paper crystals of diamond, quartz, calcite and potassium chloride (obtained from a saturated solution) were qualified as ideal. A value of $N = (6.0228 \pm 0.0002) \cdot 10^{23} \text{ mole}^{-1}$ was found.

This value is given in the chemical scale. The following molecular weights were used: diamond 12.010; quartz 60.06; calcite 100.090 and potassium chloride 74.553; see [2]. The following wavelengths of the CuK_{α_1} and CuK_{α_2} lines have been taken: 1.540516 and 1.544361 Å resp. If Cauchois' values [9] are applied (1.54051 and 1.54433 Å respectively) the value of N found by examining diamond, quartz, calcite and KCl amounts to $(6.0230 \pm 0.0002) \cdot 10^{23}$.

In the same paper selenium, various metals and single crystals of KCl (prepared by the Kryopoulou method) [3] were qualified as imperfect crystals and they showed deviations from the ideal (up to about 0.05%).

The largest deviations showed yellow PbO (rhombic crystals) and various metals. With regard to the oxide of lead it may be postulated that heat treatment at a temperature of about 700 °C causes a loss of lead (not of oxygen; cf. [4]) with the result that the density of these samples is found to be less, giving an increased value of N .

The apparent imperfection of crystals of various metals may be attributed to holes between the crystals (no mono-crystals had been prepared).

These difficulties have been overcome by SMAKULA and his co-workers [5], who examined large mono-crystals. The differences between perfect crystals and those which showed the greatest deviations (TiCl and TlBr) amounted to 0.004%.

Perfect crystals of Si, Al and CaF_2 with homopolar, metallic and heteropolar links respectively showed very good agreement in regard to the calculated value of $N: 6.02368 \cdot 10^{23} \text{ mole}^{-1}$. SMAKULA compares the imperfections (vacancies) occurring in TiCl and TlBr with those found in AgCl and AgBr.

If the density of small crystals or of a crystalline powder is determined it

is of great importance that the liquid, which is used as pycnometer liquid or as immersion liquid (floating or suspension method), does wet the solid substance. In many cases water is used as such a liquid and as it shows a high interfacial tension the wetting is poor. By replacing it by well wetting organic liquids, such as paraffin oil or petroleum, the writer has found an increase of the density of lead oxide of more than 0.5% [6]. For this reason density measurements of large crystals are preferable.

The imperfection of crystals of KCl, prepared according to the Kyropoulos method at a temperature near its melting point, followed by a relatively rapid cooling (in some hours down to about 200 °C), remains to be explained. It might be possible to relate the deviations found, to the larger number of vacancies, which are formed at high temperature. During the relatively rapid cooling the crystal is «frozen» in the state of equilibrium it has attained; it is because of this «frozen» equilibrium that the degree of imperfection has been found to be $\sim 0.02\%$ (cf. also [7]). According to WAGNER and HANTEL-MANN [8], who carried out conductivity measurements at various temperatures, the number of vacancies in KCl crystals near the melting point amounts to $1.2 \cdot 10^{-4}$, which is in good agreement with our results ($\sim 2 \cdot 10^{-4}$).

REFERENCES

- [1] N. W. H. ADDINK: *Recueil Trav. Chim. Pays Bas*, **70**, 202 (1951).
- [2] G. P. BAXTER, M. GUICHARD, O. HÖNIGSCHMID and R. WHITLAW-GRAY. *Zeits. anorg. allgem. Chem.*, **251**, 430 (1943).
- [3] S. KYROPOULOS: *Zeits. anorg. allgem. Chem.*, **154**, 308 (1940).
- [4] N. W. H. ADDINK: *Thesis Utrecht* (1933), p. 27.
- [5] A. SMAKULA, J. KALNAJS and V. SILS: *Phys. Rev.*, **99**, 1747 (1955).
- [6] N. W. H. ADDINK: *Thesis Utrecht* (1933), p. 61; E. COHEN and N. W. H. ADDINK: *Zeits. phys. Chem.*, A **168**, 207 (1934).
- [7] J. L. SNOEK: *Phil. Mag.*, **41**, 1188 (1950).
- [8] C. WAGNER and P. HANTEL-MANN: *Journ. Chem. Phys.*, **18**, 72 (1950).
- [9] K. LONSDALE: *Acta Cryst.*, **3**, 400 (1950).

Some Recent Determinations of the Velocity of Light.

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In the last decade there has been a strong development of the methods for the determination of the velocity of light. Earlier the direct methods dominated. The new ones are mainly indirect. Here ESSEN or ESSEN and GORDON-SMITH are pioneers. In 1947 they used the cavity resonator for ultra short radio-waves. These waves can most expediently be conducted in silver tubes, the diameters of which are greater than half the wave length. If the length of the tube, limited by two silver end walls, is an even multiple of half the wave length, the reflection against the end walls erects a standing oscillation in the tube. The resonance frequency of this oscillation can be calculated from the dimensions of the cavity and the velocity by which the field-variations propagate within the cavity. The dimensions and the frequency are determined with great accuracy. The only thing left, the velocity, is then calculated on basis of the known relation. If the cavity is evacuated, we get directly the vacuum value of c .

Already the first determination [1] was carried out with rare precision and skill. The cavity was here fixed. In his apparatus No. 2 of 1950 ESSEN [2] inserted a movable plunger. Thus the length of the cavity could be varied and ESSEN could detect deviations from the theoretical relation between dimensions and frequency. The accuracy was now increased by 7 or 8 times to 1 km/s and since the first result was fully confirmed, the principles applied must have been correct.

In 1950 BOL [3] also used a cavity resonator. This instrument was of the fixed type. The value differed considerably from that of ESSEN. Since the error limits were given very narrow, 0.4 km/s, this determination has caused a lot of embarrassment. From the debate there seems to be evident that the influence of the skin-effect, here only calculated, was underestimated. With experience from ESSEN's experiments, DAHYOFF has increased BOL's skin-correction from

3 to 8 km/s. Thus only by applying different points of view, BOL's result can change the value of c by km/s. I have found it best to omit this determination.

FROOME [4] used radar waves in a different method, called micro-wave interferometry. By a transmitting horn an oscillator emits waves of little more than one cm towards a reflecting movable screen, some 10 m from the horn. By the screen the waves are reflected back into the horn. Here, in a wave guide, they interfere with waves coming directly from the transmitter. An attached receiver and detector yields minimum of current when the two wave systems differ by π in phase. This will occur to every half wave length of increase of the distance to the movable reflector. The reflector is displaced totally by 1.6 m through 250 minima. This proceeding is repeated systematically at different distances from the transmitting horn. Thus disturbing reflections from objects in the room will be eliminated. The wave front shape will also be considered. In this way we get the wave length. Knowing the frequency too, we get the velocity. The result of the measurements, carried out with great care, was almost identical with that of ESSEN. Next year, 1953, FROOME [5] had ready a new considerably improved instrument. Its characteristic is a marked symmetry of the arrangements. There are two transmitter-horns, and the distance between them is 12 m. They are directed towards each other. On the line of and between the horns is the movable receiver-detector. The two emitted wave systems from the horns interfere in the receiver and the detector shows minimum of current to each half wave length of displacement of the receiver unit. 162 minima or 1 m is passed at different distances between horns and receiver. The greatest uncertainty lies in insufficient information as to the shape of the wave fronts. For two measuring series this shape was deliberately made bad. In spite of this, due to a correct treating of the conditions, these series agree with the good one, used for the final result. This fact combined with Froome's experience from his first instrument give confidence in the value obtained.

As to the remaining indirect methods I will be brief. First we have ASLASKON's «Shoran» determinations [6, 7]. The constant c is obtained by adapting Shoran distances to those geodetically known. The underlying matter is extensive. The nature of the method, however, makes the error limits a little inconveniently wide without any prospect of further reduction below 2 km/s.

In 1952 RANK, RUTH, VANDER SLUIS [8] determined the constants in the formula for the wave-length of the rotation-vibration absorption bands of HCN. They measured in infrared. The wave-length of the ground state lies in the half-cm region, where the frequency could directly be compared to an ordinary frequency standard. The determination was repeated one year later [9] with improved instruments. Then the result was 14 km/s higher. The error limits of the first determination were later on re-estimated [10] and increased by three times to ± 19 km/s.

In 1955 PLYLER, BLAINE, CONNOR [11] carried out a measurement along similar lines. The result was 2 further km/s higher or now on level with ESSEN's value. The error limits were ± 4 km/s. The rotational band-spectrum method seems not yet to have stabilized and the main signification of this very interesting experiment seems still to lie within other domains.

In the same year FLORMAN [12] used a radio-frequency interferometer. The distance was 1500 m and the wave-length 1.7 m. Up to now the method is too new and the error sources seem hard to estimate or cancel. The limits were ± 3 km/s. As for the two last methods I think the risk of unknown systematic errors is not sufficiently minimized. The jump from infrared to radar region is very large and the diffraction and scattering of 2 m waves is considerable. Regarding these cases the best is to keep awaiting.

Alongside of these indirect methods there are by now a lot of results from my direct Kerr cell method. The apparatus, the geodimeter, is used in several countries for the reverse purpose of determining geodetic distances and is checked on stringed base lines. As by Shoran these checks have yielded values on c .

The geodimeter emits a light beam, the intensity of which is modulated by a crystal controlled high-frequency radio-transmitter. The corresponding radio-wave length is 30 m. The emitted light is reflected back by a distant mirror or reflecting system and is then absorbed by a photo-tube close to the emitter. The sensitivity of the tube is high-frequency controlled by the transmitter also. Consequently the amplitude of the photo-current variates in a periodical manner with the distance to the mirror or with the time for the light to cover the distance to and fro. Since the velocity of light equals that of radio waves the period of the photo-current variation corresponds to a change of 15 m of distance (the light has to go to and fro). A particular sort of compensation circuit makes the current to pass zero two times in each period. Thus, at every $7\frac{1}{2}$ m of increased distance to the mirror the photo-current is zero. Due to the crystal control the value $7\frac{1}{2}$ is constant to within two parts in ten millions. Now, this row of zero-points to every $7\frac{1}{2}$ m is the measuring scale for the distance measurements.

By the insertion of a longer or shorter delay of the radio transmitter control of the photo-tube, the zero-point row can be moved forth or back within 8 m. Thus, wherever the distant mirror stands, a zero-point can be adjusted to coincide with the mirror. Immediately after that, with unchanged delay, the distance to the first zero-point close to the geodimeter, is determined by aid of a built in calibrated continuously variable light path or light conductor of maximum 8 m of double length. The rest of the distance, that from the first zero-point up to the last one at the mirror, is an even multiple of the $7\frac{1}{2}$ m constant.

In the first geodimeters after hard transports, the calibration of the light conductor could change with the consequence of a false distance to the first

zero-point. The error always depended on a displacement of the emission point on the photo-cathode of light from the light conductor as compared to light from the distant mirror. A side way shift of this point caused a change in transit time of the photo-electrons through the tube and to the geodimeter this was equivalent to a change of the time for the light to cover the distance to and fro. By making the recorded distance less dependent of the transit time and of changes in the light conductor the resulting errors in this year are considerably reduced. Those errors can, however, also be cancelled or *compensated* by measuring the distance as a difference between the zero-point positions of two field-mirrors. Then the light conductor is eliminated. We can also do the compensation by a complementary measurement of the distance into two parts. The last case is equivalent to a renewed calibration of the light conductor in the field. If the distance is known from the length of a base line, we get direct information of the accurate $7\frac{1}{2}$ m unit, that is of the 30 m « wave-length ». Knowing the frequency too, we obtain the velocity.

Well, in the following Table I of geodimeter results on different base lines I have selected the *compensated* determinations to get a reliable value on c .

TABLE I.

Base line		Distance (m)	Velocity (km/s)	Mean of base	Weight
Swedish [13-15]	I	6 910	299 793.02	3.05	10
	I	6 910	3.08	—	—
	II	5 400	3.17	2.80	8
	II	5 400	2.43	—	—
	III	7 320	3.37	3.37	7
Australian [16]	I	6 440	2.64	2.44	11
	I	6 440	2.05	—	—
	I	6 440	2.64	—	—
	II	9 660	2.41	2.46	14
	II	9 660	2.50	—	—
	III	6 440	3.61	3.61	3
	IV	11 100	3.21	3.21	6
Total mean: $(299\,792.85 \pm 0.16)$ km/s					

The two last measurements are *not* of the compensated type. They are, however, included in the table because they are carried out with the new improved instrument of this year, though the lack of compensation has rendered them half of weight. In this table the weights are proportionate to the product of distance and square root of the number of determination occasions. By the use of square root we have considered the errors in the base distance also.

If we regard the result from one base line, the error limits are ± 0.38 km/s. If we assume that one half of this error may come from the base and the second from the measurements, we get an accuracy of one part in a good million for each of these quantities, which seems likely.

In the following Table II are the uncompensated measurements with earlier models of the geodimeter.

TABLE II.

Base line		Distance (m)	Velocity (km/s)	Weight
Australian [16]	I	6 440	299 792.50	6
English [17]	I	11 260	2.40	11
	II	24 830	2.20	25
U.S.A. [18]	I	1 380	4.06	1
	II	12 800	4.27	13
	III	3 120	2.73	3
	IV	2 130	1.69	2
Weighted mean: (299 792.75 \pm 0.34) km/s				

The result from the Table II, with weights proportionate to the distances, may only serve as a comparison.

Now, what about the risk of systematic errors due to the common type of instrument and of measuring method? In the case of the compensated measurements there should only be three possibilities left, those of colour, of atmosphere and of base length. The effective and relatively narrow colour band is determined for each instrument according to the following proceeding: After the light has passed a calibrated variable monochromator, readings are made directly of the resulting photo-current. In the field, on account of the instrument's own filtering effect, the influence of atmospheric colour-absorption plays an insignificant role, above all at the short distances of the base lines. These lines also always are on flat country. Therefore, ordinary atmospheric conditions, temperature, pressure and humidity, are easy to determine and there is no risk of systematic errors from this domain. And from the base lines? HONKASALO [25] has shown in a careful investigation that no systematic errors are introduced by the string method during ordinary good measuring conditions.

It may now be convenient for a general summary. To get a final value on c there are, in a sense, two ways. We can take all existing values and apply weights with regard to the error limits. Or, we can select those measu-

rements weich, besides the error limits, show reason to be more reliable than the rest. From the latter point of view, as to the indirect methods, ESSEN's FROOME's and ASLAKSON's determinations inspire confidence on account of their calm and consistent development up to the final result. Thus including the extensive geodimeter measurements by several observers we arrive at the following summary listed in Table III.

TABLE III.

Method	Velocity (km/s)	Weight
Cavity resonator	$299\,792.50 \pm 1.0$	2
Micro-wave interferometry	3.00 ± 0.3	6
Shoran	3.40 ± 2.0	1
Geodimeter.	2.85 ± 0.2	8
Weighted mean.	$(299\,792.89 \pm 0.11) \text{ km/s}$	

Both of ASLAKSON's determinations are included in the Shoran value because the method is identical, only the underlying stuff is different. All values

TABLE IV.

Year	Observer	Method	Distance (m)	Frequency (MHz)	Velocity (km/s)
1947	ESSEN, GORDON-SMITH	C. R.	0.1	3 000	$299\,792 \pm 9$
1947	JONES	Oboe	70 000	3 000	782 ± 25
1948	BERGSTRAND	K. C.	9 000	8	793 ± 2
1949	HOUSTOUN	V. Q.	40	100	775 ± 9
1950	ASLAKSON	Shoran	300 000	300	792.3 ± 2.4
1950	ESSEN	C. R.	0.1	10 000	792.5 ± 1
1950	BERGSTRAND	K. C.	60 00	8	793.1 ± 0.3
1950	BOL	C. R.	0.1	3 000	789.3 ± 0.4
1952	ASLAKSON	Shoran	300 000	300	794.2 ± 1.9
1952	FROOME	M. I.	2	24 000	792.6 ± 0.7
1951	RANK, RUTH and VAN- DER SLUIS	R. S.	—	44 000	776 ± 19
1953	RANK, SHEARER and VIGGINS	R. S.	—	44 000	789.8 ± 3
1953	FROOME	M. I.	1	24 000	793.0 ± 0.3
1955	PLYLER, BLAINE and CONNOR	R. S.	—	58 000	792 ± 4
1955	FLORMAN	R. I.	1 500	173	795.1 ± 3.1
1956	Summary of geodimeter	K. C.	7 000	10	792.9 ± 0.2

In the above table the methods are abbreviated by the following symbols: C. R. = cavity resonator, K. C. = Kerr cell, V. Q. = vibrating quartz, M. I. = microwave interferometry, R. S. = rotational spectrum, R. I. = radio-frequency interferometer.

in the Table agree harmonically according to their individual error limits. Admitting a remaining common systematic error of length of ample five parts in ten millions the square root limits are increased to ± 0.2 km/s. Thus the « best » value on the velocity should be

$$c = (299792.9 \pm 0.2) \text{ km/s.}$$

The results from rotational spectrum and from radar interferometry agree with this value. There is nothing revolutionary new in the above figures as compared to recent surveys of atomic constants as given by DUMOND, COHEN a.o. or by BEARDEN and THOMSEN. Interesting is however, the good concordance between the extended geodimeter results and those obtained by indirect methods.

I add a list of determinations in the past decade (Table IV).

At last, what of further precision? FROOME has advised a still better determination with further shorter waves. As for the geodimeter method the limit mainly is the accuracy of the base. At present the most accurate length is the 864 m Väisälä interference-comparator base in Finland. The accuracy is better than one part in ten millions [25], expressed in cadmium-line waves [26]. To the geodimeter, impaired by cm-errors, the distance is too short. Using crystal modulated light of 300 MHz frequency, however, it seems possible to increase the present accuracy of c up to one part in five millions. A device for this purpose is tested in the laboratory [24].

REFERENCES

- [1] L. E. ESSEN and A. C. GORDON-SMITH: *Proc. Roy. Soc., A* **194**, 348 (1948).
- [2] L. E. ESSEN: *Proc. Roy. Soc., A* **204**, 260 (1950).
- [3] K. BOL: *Phys. Rev.*, **80**, 296 (1950).
- [4] K. D. FROOME: *Proc. Roy. Soc., A* **213**, 123 (1952).
- [5] K. D. FROOME: *Proc. Roy. Soc., A* **223**, 195 (1954).
- [6] C. I. ASLAKSON: *Trans. Amer. Geophys. Un.*, **30**, 475 (1949).
- [7] C. I. ASLAKSON: *Nature*, **168**, 505 (1951).
- [8] D. H. RANK, R. P. RUTH and K. L. VANDER SLUIS: *Journ. Opt. Soc. Amer.*, **42**, 693 (1953).
- [9] D. H. RANK, J. N. SHEARER and T. A. VIGGINS: *Phys. Rev.*, **94**, 575 (1953).
- [10] D. H. RANK: *Journ. Opt. Soc. Amer.*, **44**, (1954).
- [11] E. K. PLYLER, L. R. BLAINE and W. S. CONNOR: *Journ. Opt. Soc. Amer.*, **45**, 102 (1955).
- [12] E. F. FLORMAN: *Nat. Bur. Stand. Techn. News Bull.*, **39**, 1 (1955).
- [13] E. BERGSTRAND: *Ark. f. Fys.*, **2**, 119 (1950).

- [14] E. BERGSTRAND: *Ark. f. Fys.*, **3**, 479 (1951).
- [15] R. Ö. SCHÖLDSTRÖM: *Det. Vel. Light on Öland in 1955* (Iss. by Aga, Lidingo Sweden).
- [16] C. K. WALLER: *Cartography*, vol. **1**, no. 3 (Australia, March 1956).
- [17] I. C. C. MACKENZIE: *Ordin. Surv. Prof. Paper* (New Series), no. 19 (H. M. S. O.).
- [18] D. D. MEARS: *U. S. Army Map Service*, private communication.
- [19] E. R. COHEN and J. W. M. DUMOND: *Rev. Mod. Phys.*, **27**, 4 (1955).
- [20] J. A. BEARDEN and J. S. THOMSEN: *A Survey of Atomic Constants* (Baltimore, 1955).
- [21] F. E. JONES and E. C. CONFORD: *Journ. Inst. Electr. Engrs.*, **96**, pt. III (1948).
- [22] E. BERGSTRAND: *Ark. Mat. Astr. Phys.*, **36 A**, 20, 1949.
- [23] R. A. HOUSTOUN: *Proc. Roy. Soc. Edinburgh*, **A 61**, 102 (1941); **A 63**, 95 (1950)
- [24] E. BERGSTRAND: *Ark. f. Fys.*, **8**, 45, 457, (1954).
- [25] T. HONKASALO: *Ver. Finn. Geodet. Inst.*, no. 37 (Helsinki, 1950).
- [26] T. HONKASALO: private communication.

A Redetermination of the Value of the Faraday with the Iodine Coulometer.

(Progress Report)

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1. - Introduction.

It is certainly not necessary to remind an audience of physicists that the faraday is a very important physical constant. In physical chemistry it occurs in most expressions related to the interpretation of the results of measurements on galvanic cells, which include pH, oxidation-reduction potentials, etc. In the domain of physics the faraday has become increasingly important since the most precise method for obtaining the charge on the electron e is obtained from the relation

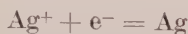
$$F = Ne,$$

in which F is the faraday, N is Avogadro's number, and e the electronic charge, which occurs, of course, in various powers in most of the equations of modern physics.

The faraday is seldom adequately defined in textbooks and books of reference. It is the number of coulombs necessary to produce one equivalent of electrochemical reaction at a metallic-electrolytic boundary, i.e., the current must pass from an electronic conductor to a purely electrolytic one or vice-versa. The condition that the conductors must be purely electronic and electrolytic is usually omitted.

In order to determine the value of the faraday it is theoretically necessary only to pass a measured number of coulombs across a metal-electrolyte boundary and measure the extent of the electrochemical reaction or reactions that have occurred. However, with an apparently almost indefinite number of possible ways of carrying this out only three methods have been found to yield an accuracy of one part in ten thousand. These are the silver coulometer, the

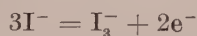
iodine coulometer, and a coulometer depending upon the reduction of sodium oxalate. Of these the silver coulometer has received by far the greatest amount of research largely because it, for many years, was the basis for the definition of the ampere. An adequate discussion of the strengths and failings of the silver coulometer would take us too far afield at this point. Three difficulties with the instrument may be mentioned: (a) It has not been possible to show that the reactio



is strictly reversible, (b) inclusions of solution in the deposited silver have been demonstrated, and corrections are difficult, and (c) silver has two isotopes present in approximately equal amounts and selective deposition of one or the other is probable. In addition it is relevant to recall that the work on this instrument was carried out mostly fifty years ago.

A careful research has been carried out by CRAIG and HOFFMAN [1] in which the electrochemical reaction studied was the reduction of sodium oxalate. This coulometer shares with the silver instrument the weakness that the reaction is not reversible, and there are difficulties concerning the isotopic composition and atomic weights of the substance involved. The study should, however, certainly receive further attention.

This leaves the iodine coulometer the subject of this discussion. The electrochemical reaction on which this instrument depends is



at an anode, and the reverse of this reaction at a cathode. The classical work on the iodine coulometer was carried out over forty years ago by WASHBURN and BATES [2] and by BATES and VINAL [3]. There are several decided advantages in using this electrochemical reaction for obtaining the faraday. Iodine has no isotopes, i.e., occurs only in one electronic state. Its atomic weight is accurately known. It can be prepared in a state of high purity. The electrochemical reaction being reversible, both the anode and cathode reactions may be used. Since the reactants are in solution there is no question of inclusions. The difficulties encountered with the method have been related to the volatility of iodine and in making the chemical analysis sufficiently accurate.

The faraday F is defined by the relation

$$(1) \quad F = \frac{QA}{m},$$

in which m is the mass of the substance entering into electrochemical reaction,

A is the equivalent weight (the atomic weight for the iodine coulometer) and Q is the number of coulombs passed across the electrode surface. If the current is constant

$$Q = It,$$

in which I is the current in amperes and t is the time in seconds, then equation (1) becomes

$$F = \frac{AIt}{m}.$$

Since it is convenient to determine the current from standard cells of potential E and standard resistances of value R we obtain

$$F = \frac{AEt}{mR}.$$

The problem of obtaining a value of the faraday from an electrochemical reaction for which the relevant equivalent weight is known is (a) to find the mass m from a sufficiently accurate analytical method, (b) to maintain a constant current, determined by the values of the potential E and the resistance R , both of which must be known to the accuracy desired, and (c) the time, t , during which the electrolysis is carried out, must also be precisely determined. In practical terms this means that there must be available a coulometer, a method of analysis, a constant current apparatus, and a device for measuring time. These will be described in the order given.

2. - The coulometer.

The design of the coulometer adopted is shown in Fig. 1. The arrangement allows for the formation of free iodine by the reaction

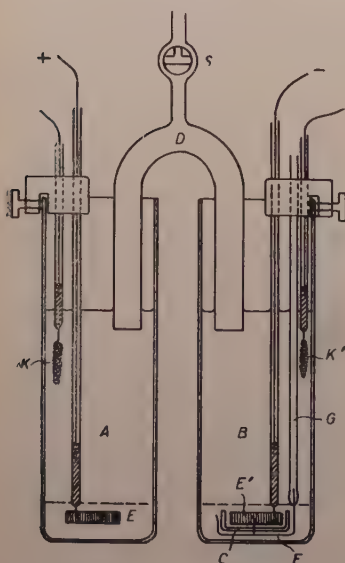


Fig. 1.

in the anode vessel A , and the reverse reaction in the cathode chamber B . During the passage of current the two vessels are connected by an electrolytic conductor in the bridge tube D . After the electrolysis the stop cock S is opened with the result that the connecting electrolyte runs into the electrode vessels. The free

iodine is then titrated in the two electrode compartments by the method to be described below.

Since free iodine can form from iodides in the presence of oxygen, and because it is necessary to keep the iodide concentration low to obtain good electrometric end points for the titrations, a solution of potassium chloride has been interposed, between the electrode solutions; thus the system may initially be represented by



The anode *E* consists of a spiral made of 45 cm of thin platinum foil 5 mm wide. The separate turns of the foil are kept in place by four platinum wires that pass through diameters of the spiral. In the cathode portion a similar platinum spiral *E'* is placed in a glass cup *C* by means of which a weighed amount of solid iodine is introduced. The cup is lowered into the vessel by a basket *F*, made of platinum wires, which is supported by the tube *G*.

The glass cup *C* which is used for introducing weighed amounts of solid iodine into the cathode region needs further description. The cups have been made by cutting off the bottoms of pyrex beakers, and optically polishing the exposed edges. These are fitted with covers, also optically polished. At the contact of cover and cup interference fringes are visible. When iodine is placed in such a cup and covered the loss of iodine through the annular contact is negligible. In practice the cup and circular cap are held together for convenient handling with a clip. After weighing the cup and clip are placed in a covered vessel which is in turn placed on a surface of «dry ice». This reduces the vapor pressure of iodine nearly to zero. It is in this chilled condition that the iodine is placed in the coulometer. Tests with starch paper, which is exceedingly sensitive, indicate that no iodine remains with the cover, which is removed.

The auxiliary electrodes *K* and *K'* will be discussed in connection with the constant current apparatus to be described below.

3. - The analytical method.

The method employed for determining the free iodine in solution is differential electrometric titration, which has proved to be highly accurate in acidimetry [5] and in the determination of chlorides [6]. The procedure differs from direct electrometric titration in that, when nearing the end point, a portion of the titrated fluid, containing an electrode, is held from reaction while an increment of reagent is added to the body of the solution which holds another electrode. The difference in potential between the two electrodes goes through a maximum at the end point. This is easier to locate than the point

of inflexion observed with the direct titration. Furthermore, no reference electrode, which may introduce errors, is necessary.

The apparatus with which the titrations is carried out is shown in Fig. 2. The vessel *A* contains the solution to be titrated. As will be seen it also serves

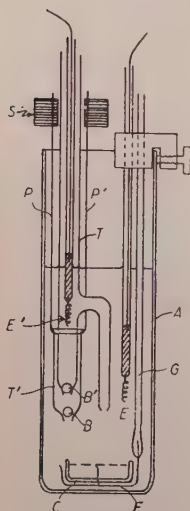


Fig. 2.

as one of the electrode vessels of the coulometer, thus avoiding transfer of the solution. The body of the solution holds the electrode *E*, which may be the anode or cathode, and another electrode *E'*, is placed in the tube *T*. This tube fits snugly into the tube *T'* which is suspended by the platinum wires *P-P'* from the support *S*, through which the tube *T* passes freely. At the bottom of tubes *T* and *T'* are small holes over which are placed the glass balls *B* and *B'*. Circulation of solution past the electrode *E'* can be obtained by grasping the tube *T* at its upper end and moving it up and down. A few strokes are sufficient to produce thorough mixing with the body of the solution. Unless circulation is desired the fluid around the electrode *E'* is not disturbed by stirring, which is accomplished with a helical stirrer, not shown.

The procedure followed in calibrating the titrating solution is as follows. About 2 g of solid iodine are placed in the weighing cup, a cover and clip applied, and the combination carefully weighed on the microbalance, after which it is placed in a covered vessel on dry ice to chill. It is then transferred to the wire basket *F* and lowered into the vessel *A* into which 5 g of potassium iodide have been placed. The cover of the weighing cup is then removed with a rubber suction disk, after which about 25 ml of the potassium chloride solution are added. With slight agitation the iodine dissolves. More of the potassium chloride solution is added to about 150 ml. The titration with thiosulphate solution (about $\frac{1}{3}$ normal) is then commenced, using a weight burette.

The titration involves three stages. (a) With the tube *T* of the pump undisturbed, the thiosulphate solution is added to the body of the solution. The iodine color in the body of the solution nearly or entirely disappears. (b) The pump is then operated and the potential returns to zero. The titrating fluid is added drop by drop, with pumping after each addition, until a potential of 10 to 15 mV is observed. (c) With a solution diluted so that 1 ml contains a known weight (about 10 mg) of the strong solution, the differential titration is continued, drop by drop. A clear maximum value indicates the end of the titration, with a sensitivity of one part in 10^5 .

In order to effect a valid calibration of the solution, and to furnish a known quantity of iodine for cathode reduction in the coulometer it is necessary to have that element in a state of adequate purity. This has been attained by

repeated sublimation. The method used has been to place a dish containing a mixture of solid iodine and potassium iodide in a bell jar resting on a glass base. In the upper end of the jar is an electric light which shines on the mixture. Crystals of iodine form slowly on the lower sides of the bell jar, and may be conveniently scraped out as desired. The effectiveness of this procedure is shown from an investigation carried out by Dr. R. W. DODSON and associated at the Brookhaven National Laboratory. Using activation analysis the ratios $\text{Cl/I} = .5 \cdot 10^{-6}$ and $\text{Br/I} = .08 \cdot 10^{-6}$ were found. We are most grateful for this collaboration.

In using the microbalance the weights employed were checked against standards calibrated by the Bureau of Standards.

4. - The constant current apparatus.

In its simplest elements the constant current device now in use is shown in Fig. 3. The coulometer C is connected in series with storage cells, S , the standard resistance R_1 , and the adjustable resistance R_2 . In parallel with R_1 are the standard cell W and the galvanometer G . Light from the lamp filament F passes through the lens L to the galvanometer mirror and an image of the filament is focussed on the differential photo-cells D . Motion of the light spot on these cells operates the relay P which controls the direction of rotation of the reversing motor M , producing small alterations of the resistance R_2 . Thus the current through the coulometer is continually in process of adjustment to a value determined by the potential of the standard cell W and the standard resistance R_1 .

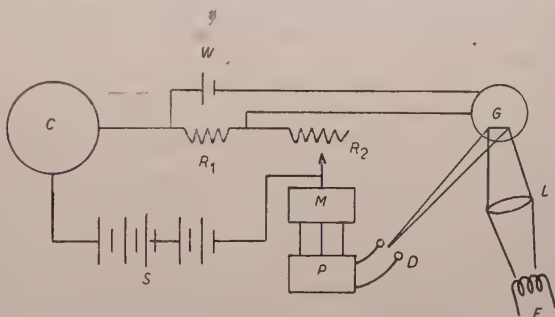


Fig. 3.

The actual apparatus is complicated by the fact that it must be operating with the desired current flowing through an auxiliary resistance up to the instant of commencing the electrochemical reactions in the coulometer. Provision must also be made for automatic opening of the circuit containing the galvanometer and standard cell in case of any failure of the apparatus.

The changes of resistance and electromotive force which occur during the passage of current through the coulometer must be compensated if the current is to remain constant. Since comparatively slight deviations of the light spot from a point between photo-cells D of Fig. 3 can result in failure of the oper-

The standard resistance, R_1 , is connected in series with the saturated Weston standard cell, W , the galvanometer, G , and one of the blades of the switch SW_1 .

Automatic adjustment of the variable electrolytic resistance, R_3 , to yield a constant current through the coulometer is accomplished as follows: light from the lamp filament, Fi , is focussed, by the lens, L , and the mirror of the galvanometer, G , normally on a line between the cadmium sulphide photo-conductive cells, A and B . These cells are in a bridge system including as the other arms the resistances, E and F . Any deviation of the current through the main circuit from that determined by the standard resistance, R_1 , and the standard cell, W , will cause the galvanometer G to deflect the line of light to one of the photo-cells, A or B . If to cell A , this will impress a potential on the grid of the tube T in phase with the plate voltage so that current passes which operates the relay K , with the result that the Hayden reversing motor turns to produce an increase of the resistance of the electrolytic rheostat, R_3 , thus diminishing slightly the current of the principal circuit and causing the galvanometer mirror to shift the reflected line of light from photo-cell A to cell B . In this condition the potentials impressed on the grid will be out of phase with the plate voltage of the tube T . This in turn changes the contact of the relay, K , so that the motor, H , operates in the opposite direction. Thus the electrolytic rheostat, R_3 , is continually receiving slight adjustments to maintain the current constant. A difference of potential of about five microvolts will cause the motor, H , to reverse its direction. Since the standard cell, W , has a potential of about one volt, the regulation, as now used, is of the order of five parts in a million.

To protect the galvanometer and the standard cell in case of any failure in the apparatus, provision is made to release the contacts of the relay, P , in case the light reflected from the galvanometer mirror reaches the photo-cells, C or D . Normally current passes through the tube, V , holding the contacts of the relay, P , in closed position. However, illumination of C or D will change the grid potential of the tube, V , thus effecting the release of these contacts with the result that the galvanometer circuit is opened, and the motor, H , is stopped.

As already stated, it is necessary for the purpose of this research that current be passing through the principal circuit, with the value determined by the quotient of the values of the potential of the standard cell and the standard resistance, R_1 , at the moment at which the current is started through the coulometer. To meet this requirement the switch SW_1 is turned to the right, so that the current is passing through the variable resistance, R_4 , which must have a resistance equal to that of the coulometer, C . In order to make the appropriate adjustment a bridge system is provided by opening switch SW_1 and closing switch SW_2 . A source of audio frequency current from the generator, Q , is impressed on the bridge as shown and since the resistance arms I

and J are both $100\ \Omega$, equality of resistance, Co and R_4 , is indicated by a minimum of sound in the telephone, N . The switch SW_2 is then opened, and SW_1 is closed to the right until it is desired to pass current through the coulometer, when it is turned to the left.

Since the range of resistance through which the constant current apparatus will operate is limited, and the rate at which this resistance can be adjusted is also restricted, it has been found desirable to heat, by alternating current, the bridge tube D of Fig. 1, before the electrolysis occurs. This is done with the aid of the platinum electrodes K and K' of that figure which are placed in the potassium chloride solution away from the region of the electrodes. The same current in a.c. as the d.c. which is used in the electrode reactions. Relatively small changes of resistance occur after this preliminary heating.

5. - The standard cells.

We have been more than fortunate in the co-operation of Dr. M. EPPLEY and the Eppley Foundation in making available to us a set of saturated Weston standard cells. The calibration of these cells by the Bureau of Standards at 30° had the following result

	Electromotive force
1	1.018 119 V
2	1.018 119 »
3	1.018 119 »
4	1.018 120 »
5	1.018 119 »
6	1.018 118 »

We will also be indebted to the same source of a comparator for working with these cells.

6. - The time measurement.

Time signals are broadcast from the National Bureau of Standards by Radio Station WWV. Pulses at intervals of precisely one second are received in our laboratory and recorded on a magnetic tape recorder. The starting and stopping of the current for the electrolysis are also recorded on the tape by the use of a high frequency buzzer, operated by a relay in the circuit. Fractions of a second can be estimated with high accuracy by means of an expedient originating with PASQUINELLI [6] and FRINGS and FRINGS [7]. In this pro-

cedure the recorded surface is drawn through a thin layer of finely divided iron powder and the excess blown off. The magnetic record is clearly visible, and the spacing between the different events easily measured.

7. - Conclusions.

As stated in the title this is a progress report. We have no values of the faraday to propose at the present time. However, the problems connected with an accurate determination of that important constant appear to have been solved. It now remains to make sufficient experiments, changing all the relevant variables, so that a statistically acceptable value of the constant will be obtained.

REFERENCES

- [1] D. N. CRAIG and J. I. HOFFMAN: *Electrochemical Constants*, p. 13; *Nat. Bur. Stand.*, Circular 524; *Phys. Rev.*, **80**, 487 (1950).
- [2] E. W. WASHBURN and S. J. BATES: *Journ. Am. Chem. Soc.*, **34**, 1341 (1912).
- [3] S. J. BATES and G. W. VINAL: *Journ. Am. Chem. Soc.*, **36**, 916 (1914).
- [4] D. A. MACINNES and I. A. COWPERTHWAIT: *Journ. Am. Chem. Soc.*, **53**, 555 (1931).
- [5] D. A. MACINNES and M. DOLE: *Journ. Am. Chem. Soc.*, **51**, 1119 (1929).
- [6] F. PASQUINELLI: *L'Acoustique des Orthoptères*, (Paris, 1955) p. 50.
- [7] H. FRINGS and M. FRINGS: *Nature*, **178**, 328 (1956).

A Precise Measurement of the Magnetic Moment of the Proton.

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The value of the magnetic moment of the proton in nuclear magnetons plays an important part in the determination of the best value of the fundamental atomic constants, particularly in the recent determinations by DUMOND and his co-workers [1, 2]. Until recently two measurements of this quantity had been made by HIPPLE *et al.* [3] and by JEFFRIES [4]. The results they quoted were

HIPPLE *et al.*: $\mu_p = (2.792\,76 \pm 0.000\,06)$ nuclear magnetons,

JEFFRIES: $\mu_p = (2.792\,4_5 \pm 0.000\,2)$ nuclear magnetons.

The lack of agreement between these values was a matter of some concern, though the analysis presented by DUMOND *et al.* in their 1955 adjustment of the values of the fundamental constants [2] favoured the value quoted by HIPPLE.

These measurements were made by the application of a method originally proposed by ALVAREZ and BLOCH [5], who pointed out that the ratio of the proton spin precession frequency ν_n in a magnetic field H to the proton cyclotron frequency ν_c in a magnetic field H' gives the magnetic moment of the proton μ_p in nuclear magnetons by the relation

$$\mu_p = \frac{\nu_n}{\nu_c} \cdot \frac{H'}{H}.$$

This principle has been used to measure μ_p with greater precision than the two previous measurements, using a modification of the «inverted cyclotron» technique of JEFFRIES for the determination of ν_c .

In practice the measurements of ν_n and ν_c were made simultaneously in

a magnetic field where, apart from a small correction due to field inhomogeneities, $H = H'$, so that μ_p is simply the ratio ν_n/ν_c . The magnet used has a 2.5 cm gap between polepieces 28 cm in diameter. The pole faces were ground flat to within optical tolerances and it was found possible to obtain a magnetic field homogeneous to ± 1 part in 60 000 over a circular region 12 cm in diameter without the use of shims. The magnetic field was stabilized using a proton resonance signal to control the current to the energizing coils. By using techniques which are now well established, it was possible to measure the value of ν_n in a water sample (which, due to the diamagnetism of the water molecules, needed to be corrected to obtain the value of ν_n for the free proton) to at least 1 part in 100 000.

The measurement of ν_c is less precise than the measurement of ν_n for two reasons. First, it is difficult to obtain sharp cyclotron resonance peaks, and, second, it may be difficult to find the true value of ν_c from the observed peaks. The electrode geometry used for decelerating a beam of protons injected at an energy of 9.5 keV is shown in Fig. 1. In the magnetic field used, about 2350 G, $\nu_n = 10$ MHz and ν_c was about 3.58 MHz. A source of alternating

voltage V_d at a frequency ν_d , variable in the region of the 8-th harmonic of ν_c , was connected between the two outer earthed electrodes and the straight-sided central electrode. The width of the central electrode was arranged so that the initially injected protons, travelling in an orbit of 6 cm radius, crossed the central conductor in somewhat less than one cycle of the voltage. Some of the protons consequently received a net deceleration and moved in an orbit of smaller radius. At a radius of 4 cm the time taken to cross the central electrode was just one cycle, consequently the protons would have received no net deceleration and could never have reached an orbit of smaller radius. In practice the 4 cm radius orbit was approached only when ν_d was very nearly the 8-th harmonic of ν_c . By placing a current collecting probe just outside the 4 cm orbit and varying ν_d near $8\nu_c$ current peaks were observed from which a value of ν_c could be deduced. The width of these peaks varied with the value of V_d in a manner shown in Fig. 2. The narrowest peaks, of which an example is shown in Fig. 3, were 1 part in 16 000 wide at the base.

The theory of the motion of the protons in this electrode geometry has been developed to account for the observed variation of the peak width with the value of V_d . The important fact shown by the theory is that the true

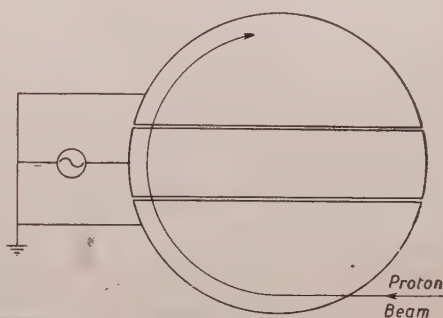


Fig. 1. — Electrode geometry. The beam travels into an electrode system similar to cyclotron dees, but split as shown.

value of ν_c always lies within the observed peak, and between the centre and the lower frequency limit of the peak. Consequently it is possible to obtain

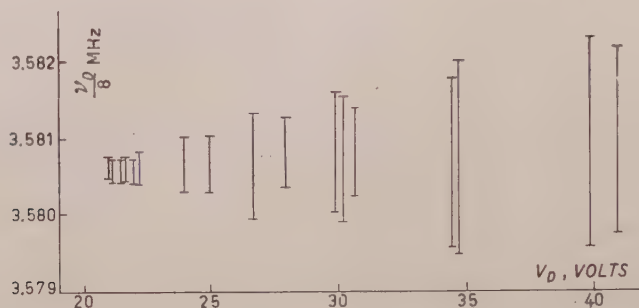


Fig. 2. — Peak widths at base, taken with the probe at a radius of 4.55 cm.

a value of ν_c with an estimated limit of error of ± 1 part in 100 000. When other sources of error are taken into account the value of the magnetic moment of the proton obtained, with the estimated limit of error, is

$$\mu_p = (2.792\,81 \pm 0.000\,04) \text{ nuclear magnetons.}$$

This value has been obtained by applying a correction of 28 parts per million to the observed value of ν_n to take account of the diamagnetism of the water sample.

Since these measurements were made TRIGGER has repeated JEFFRIES' work and has developed the theory of the motion of the protons in the inverted cyclotron. The theory involves a modification of the method of obtaining the value of ν_c from the observed current peaks and the result quoted by TRIGGER [6] is

$$\mu_p = (2.792\,75 \pm 0.000\,10) \text{ nuclear magnetons.}$$

This figure is in agreement with the result quoted above, and with HIPPLE's value; it

appears that the value of the magnetic moment of the proton must lie close to 2.792 78 nuclear magnetons.

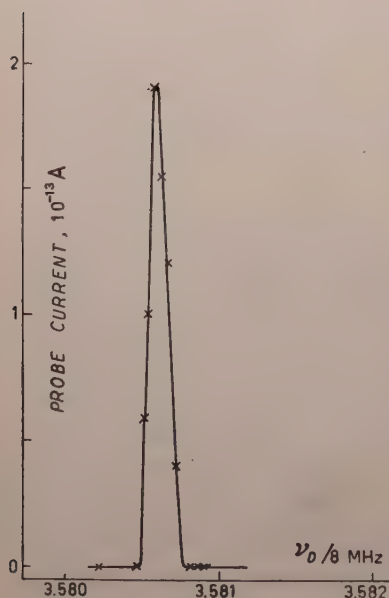


Fig. 3. — Typical peak, taken at a probe radius of 4.55 cm and at $V_D = 21.5$ V.

REFERENCES

- [1] J. W. M. DuMOND and E. R. COHEN: *Rev. Mod. Phys.*, **25**, 691 (1953).
- [2] E. R. COHEN, J. W. M. DuMOND, T. W. LAYTON and J. S. ROLLETT: *Rev. Mod. Phys.*, **27**, 363 (1955).
- [3] H. SOMMER, H. A. THOMAS and J. A. HIPPLE: *Phys. Rev.*, **82**, 697 (1951).
- [4] C. D. JEFFRIES: *Phys. Rev.*, **81**, 1040 (1951).
- [5] L. W. ALVAREZ and F. BLOCH: *Phys. Rev.*, **57**, 111 (1940).
- [6] K. R. TRIGGER: *Bull. Am. Phys. Soc.*, II, **1**, 220 (1956).

Eine Neubestimmung des Gyromagnetischen Verhältnisses des Protons.

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Ein Atomkern vollführt im magnetischen Feld eine Präzessionsbewegung. Die Kreisfrequenz dieser Präzession, die sog. Larmorfrequenz beträgt

$$\omega = \frac{\mu}{P} H,$$

wenn μ das Kernmoment und P der Kernspin ist. Der Quotient μ/P wird als gyromagnetisches Verhältnis bezeichnet und ist eine für jeden Kern charakteristische Konstante. Gemäß der obigen Beziehung erfolgt die Bestimmung des gyromagnetischen Verhältnisses durch Messung der Larmorfrequenz und der magnetischen Feldstärke. Dann ist

$$\gamma = \frac{\omega}{H}.$$

Damit ist die zu bestimmende Größe auf zwei meßbare zurückgeführt. Zur Messung der Larmorfrequenz eignen sich hervorragend die Kernresonanzverfahren, wie sie von BLOCH *et al.* als Kerninduktion und von PURCELL *et al.* als Kernabsorption beschrieben worden sind. Das Wesentliche dieser Methoden besteht darin, daß die Kerne einem zusätzlichen hochfrequenten Wechselfeld ausgesetzt werden, das senkrecht zum statischen Magnetfeld auf die Kerne einwirkt. Fällt die Frequenz dieses Wechselfeldes mit der Larmorfrequenz zusammen, so erweitern sich die Präzessionskegel der Kerne zu Präzessions Ebenen und die Präzessionen erfolgen gleichphasig.

Die Meßanordnung von BLOCH besteht darin, daß in einer ersten Spule, die die Probe umgibt und deren Achse in x -Richtung liegt, das hochfrequente

Wechselfeld erzeugt wird und in einer zweiten Spule, deren Achse in y -Richtung liegt, durch das von den präzedierenden Kernen ausgehende Wechselfeld eine Spannung induziert wird, die verstärkt und gleichgerichtet wird. Da die beiden Spulen infolge ihrer zueinander senkrechten Anordnung voneinander entkoppelt sind, läßt sich trotz der Anwesenheit des $2 \cdot 10^6$ stärkeren H_x -Feldes das Kernsignal nachweisen.

Die PURCELL'sche Anordnung zum Nachweis der Kernabsorbtion benutzt den Umstand, daß die Kerne im Resonanzfall in energetisch höhere Zustände übergehen. Die dazu erforderliche Energie entnehmen die Kerne dem hochfrequenten Wechselfeld, was eine zusätzliche Dämpfung des dieses Feld erzeugenden Schwingkreises bewirkt. Diese Dämpfung wird in einer Brückenschaltung nachgewiesen.

Der von uns verwendete Resonanz-Detektor stellt eine Modifikation des Robert'schen Superregenerativ-Oszillators dar und wird weiter unten beschrieben.

Von allen Kernen verdient das gyromagnetische Verhältnis des Protons das größte Interesse, weil das Proton gewissermaßen der Standard-Kern ist, auf den die gyromagnetischen Verhältnisse der anderen Kerne bezogen sind. Außerdem eröffnet die Kernresonanz-Methode ein bequemes Verfahren zur Messung magnetischer Feldstärken, die dabei mit der gleichen Genauigkeit bestimmt werden können, mit der das gyromagnetische Verhältnis bekannt ist. Schließlich ergeben sich durch Kombination mit anderen Meßergebnissen weitere fundamentale Konstante.

Bisher wurde das gyromagnetische Verhältnis des Protons nur einmal präzise gemessen, und zwar 1950 von THOMAS, DRISCOLL und HIPPLE im National Bureau of Standards. Dabei wurde die Larmorfrequenz nach der Absorptionsmethode und das etwa 5 000 Gauß starke Feld des Elektromagneten mit einer Cotton-Waage gemessen. Das Ergebnis lautet:

$$\gamma' = (2.675\,23 \pm 0.000\,06) \cdot 10^4 \text{ s}^{-1} \text{ G}^{-1} \quad (\text{diamagnetisch unkorrigiert})$$

$$\gamma = (2.675\,28 \pm 0.000\,06) \cdot 10^4 \text{ s}^{-1} \text{ G}^{-1} \quad (\text{diamagnetisch korrigiert})$$

$$\gamma = (2.675\,30 \pm 0.000\,06) \cdot 10^4 \text{ s}^{-1} \text{ G}^{-1} \quad (\text{diamagnetisch korrigiert auf Grund neuerer Untersuchungen})$$

Wie die Fehlerdiskussion der Autoren zeigt, ist die Messung der Feldstärke rund zehn mal ungenauer als die Messung der Larmorfrequenz. Diese Tatsache deutet schon darauf hin, daß der Genauigkeit des Ergebnisses in erster Linie durch die Unsicherheit der Feldmessung eine Grenze gesetzt ist. Deswegen erstrebten wir bei der Neubestimmung des gyromagnetischen Verhältnisses eine Meßanordnung, die bei realisierbarem Aufwand größtmögliche Genauigkeit erlaubt. So erzeugten wir das Magnetfeld in einer eisenfreien Spule und be-

rechneten die Feldstärke aus den Spulendimensionen und dem durchfließenden Strom. Dadurch wird die Zahl der Fehlerquellen verringert. Zudem wird bei geeigneter Formgebung der Spule (Länge \gg Durchmesser) das Feld im Spulenzentrum hinreichend homogen; die noch verbleibende Inhomogenität läßt sich berechnen.

Diesem Vorteil auf der magnetischen Seite steht aber zunächst ein Nachteil auf der kernresonanztechnischen Seite gegenüber. Die obere Grenze der Feldstärke eines Präzisions-Solenoiden liegt in der Größenordnung von 100 G. Dies bedingt gegenüber den üblichen Feldstärken von einigen tausend Gauß ein erheblich schwächeres Kernsignal, da dessen Größe etwa proportional dem Quadrat der Feldstärke ist. Das dadurch verursachte schlechte Signal:Rausch-Verhältnis könnte die Meßsicherheit der Larmorfrequenz beeinträchtigen. Die räumliche Vergrößerung der Protonenprobe ist nur insoweit sinnvoll, als man dadurch keine inhomogen Feldbereiche mit in das Probenvolumen einbezieht. Statt dessen wurde erstrebt, den Rauschpegel möglichst niedrig zu halten, was sich durch Arbeiten mit extrem schmaler Bandbreite erreichen läßt. Es wurde deswegen auf die übliche « Wobbelung » verzichtet, die darin besteht, daß die Frequenz oder die Feldstärke niederfrequent periodisch um den Resonanzwert herum variiert wird, wobei der sich ständig wiederholende Resonanzdurchgang im Oszillographen z.B. als Resonanzkurve sichtbar gemacht werden kann. Dazu ist eine Bandbreite erforderlich, die ein Mehrfaches der Wobbelfrequenz, also einige 100 Hz beträgt. Statt dessen wurde der Resonanz-Detektor so ausgelegt, daß er den Resonanzzustand statisch anzuzeigen vermag. Durch Verwendung langer Zeitkonstanten wurde dabei eine Bandbreite von etwa 1 Hz erreicht; anschaulich ausgedrückt: die Komponenten des Rauschspektrums über 1 Hz werden unterdrückt. Dadurch wurde bei einem Probenvolumen von 1 cm³ Wasser ein Signal:Rausch Verhältnis von 50:1 erzielt.

Das magnetische Feld wurde in einer Spule von ca. 1 m Länge und 6 cm Durchmesser erzeugt. In ein vorgeschchnittenes Gewinde sind 796 Windungen 1 mm starken, baumwollisolierten Kupferdrahtes eingelegt. Ein Ende der Wicklung ist mit dem Messing-Spulenkörper verlötet, so daß der Strom am anderen Ende durch eine bifilare Leitung zugeführt werden kann, wodurch Störfelder, die von getrennten Zuleitungen ausgehen würden, vermieden werden. Der Spulenkörper ist doppelwandig ausgeführt; der Raum zwischen den Wänden wurde von Kühlwasser durchflossen, wodurch bei den Messungen eine konstante und definierte Spulentemperatur gewährleistet ist. Bei der Auswertung der Messung wurde als Spulentemperatur das Mittel zwischen Einfluß- und Ausflußtemperatur zu Grunde gelegt, deren Differenz etwa 1 °C betrug.

Die Messung der Spulenlänge erfolgte mittels Mikroskop und Glasmaßstab, der in der PTB geeicht wurde. Da die textilumspunnenen Windungskanten nur ungenau zu fixieren sind, wurde nahe den beiden Spulenden je ein feiner Draht in die Windungsrillen eingezogen, dessen Kante als Bezugspunkt für

die Längenmessung diente. Nach jeder Meßreihe wurde die Lage dieser « Visierdrähte » geändert, damit sich die Ungenauigkeiten infolge der ungleichmäßig dicken Umspinnung des Spulendrahtes wegmittelten. Die bei jeder Meßreihe erfaßte Windungszahl wurde ausgezählt und die gemessene Teillänge entsprechend der vollen Windungszahl (796) extrapoliert. Die so gemessene Länge betrug bei 20 °C

$$L_{20} = 99.470 \pm 0.002 \text{ cm} .$$

Sie ist jedoch nicht ganz verbindlich, weil eine genauere Untersuchung zeigte, daß die Windungsdichte auf der Spule nicht konstant ist. Es wurde daher die Windungsdichte als Funktion des Ortes längs der Spule gemessen. Um die « effektive » Länge der Spule zu ermitteln, wurde eine Mittelwertbildung so vorgenommen, daß die einzelnen Spulenpartien mit verschiedenem Gewicht in die Mittelwertbildung eingehen, wobei die Gewichtszahl einer Spulenpartie proportional dem Feldstärkeanteil sein muß, mit dem die betreffende Partie zum Gesamtfeld im Zentrum beiträgt. Die so errechnete « effektive » Länge ergab

$$L_{20 \text{ eff}} = 99.468 \pm 0.002 \text{ cm} .$$

Der Durchmesser der Spule betrug

$$D = 6.100 \pm 0.002 \text{ cm} .$$

Für die Feldstärke im Zentrum einer Zylinderspule gilt:

$$H = \frac{0.4\pi n}{\sqrt{L^2 + D^2}} I = k \cdot I \text{ G} .$$

Berücksichtigt man, daß die Spule bei einer Betriebstemperatur von 15 °C eine Länge von

$$L_{15} = 99.459 \text{ cm}$$

hat, so ergibt sich die Spulenkonstante

$$k = 10.0384 \text{ G A}^{-1} .$$

Der Spulenstrom wurde von Hand mittels einer Grob- und elektronischen Feinregelung auf einen solchen Wert eingestellt, daß sein Spannungsabfall an einem Normalwiderstand gegen die Spannung eines Normalelementes kompensiert war, was durch Stromlosigkeit des im Kompensationskreis liegenden

Spiegelgalvanometers angezeigt wurde. Der 0.1Ω -Normalwiderstand war in einem Petroleum-Umlauf-Thermostaten untergebracht, dessen Temperatur maximale Schwankungen von $\pm 0.04^\circ\text{C}$ um den Sollwert von 20°C aufwies. Die Eichung des Normalwiderstandes erfolgte zuvor bei der PTB im selben Thermostaten und unter gleicher Strombelastung wie bei den Messungen. Die Weston-Elemente befanden sich in einem Luft-Thermostaten, waren in der PTB geeicht und wurden während der Messungen mehrmals untereinander verglichen. Normalelement und Normalwiderstand hatten folgende Werte:

$$U_N = 1.01864 \quad \text{abs. V,}$$

$$R_N = 0.1001502 \quad \text{abs. } \Omega.$$

Der Spulenstrom betrug also $I = U_N/R_N = 10.17112$ abs. A und die Feldstärke $H = k \cdot I = 102.102$ G.

Der Fehler der Spulenkonstante setzt sich zusammen aus dem Fehler der Länge und dem Fehler des Durchmessers. Eine Berechnung der Fehlerfortpflanzung ergibt, daß der relative Fehler der Länge voll eingeht, während der relative Fehler des Durchmessers im Quadrat des Längen:Durchmesser-Verhältnisses reduziert wird. Letzterer beträgt demnach 10^{-6} und braucht wegen seiner Kleinheit nicht weiter berücksichtigt zu werden.

Der relative Fehler der Spulenkonstanten beträgt also

$$\frac{\Delta k}{k} = 2 \cdot 10^{-5}.$$

Die Eichwerte von Normalelement und Normalwiderstand sind auf je $1 \cdot 10^{-5}$ gewährleistet, so daß die Fehlergrenze der Feldbestimmung $\pm 4 \cdot 10^{-5}$ veranschlagt werden kann.

Entwickelt man den Ausdruck für die Feldstärke in Abhängigkeit vom axialen bzw. radialen Abstand vom Zentrum, so ist zu ersehen, daß die relative Inhomogenität innerhalb des Probenvolumens höchstens $\pm 2 \cdot 10^{-6}$ beträgt.

Dem Eigenfeld $H = k \cdot I$ der Spule ist stets das erdmagnetische Feld überlagert. Die Spule war so aufgestellt, daß ihre Achse in Richtung des Erdfeldes lag. Wurde nun das Spulenfeld im Verlaufe einer Meßreihe umgepolt, so wurde der Einfluß des Erdfeldes eliminiert: Es seien ω_1 und ω_2 die bei je einer Spulenfeldrichtung gemessenen Resonanzfrequenzen. Dann gilt:

$$\omega_1 = \gamma(H + H_E)$$

$$\omega_2 = \gamma(H - H_E)$$

$$\frac{\omega_1 + \omega_2}{2} = \gamma \cdot H.$$

Bei der Auswertung der Messung ist also mit dem Eigenfeld H und dem arithmetischen Mittel der beiden Resonanzfrequenzen zu rechnen. Eine kurze Rechnung ergibt, daß die Einstellung der Spule nicht kritisch ist. Weicht die Spulenrichtung z.B. um 10° von der Richtung des Erdfeldes ab, so ergibt sich ein systematischer Fehler von nur $2 \cdot 10^{-7}$.

Der Resonanzdetektor besteht im wesentlichen aus einem Oszillator, dessen Schwingspule außerhalb des Gerätes im Zentrum der Feldspule liegt und die Protonenprobe enthält. Die Frequenz des Oszillators ist zwischen 430 und 440 kHz fein abstimmbar. Ein sehr hochohmiger Gitterableitwiderstand bewirkt, daß die hochfrequenten Schwingungen nicht kontinuierlich erfolgen. Vielmehr entsteht durch periodische Gitterblockierung, d.h. durch negative Sperrspannung, die im schwingenden Zustand der Gitterstrom am Gitterableitwiderstand erzeugt, eine impulsförmige Modulation der hochfrequenten Schwingung. Auf einen Impuls von 0.3 ms Dauer folgt eine Impulspause von 2.5 ms. Wird nun in der Schwingspule eine HF-Spannung induziert, so bewirkt diese durch ihren Einfluß auf den Anschwingvorgang, daß die Impulshöhe größer wird und die Schwingungen jeweils früher einsetzen, d.h. die Impulsfolge-Frequenz nimmt zu. Beides bedeutet eine Erhöhung der vom Oszillator erzeugten mittleren HF-Spannung. Die präzedierenden Protonen bewirken einen solchen Induktionseffekt, wenn ihre Larmorfrequenz gleich der Oszillatorfrequenz und ihre Relaxationszeit größer als der Abstand zweier aufeinanderfolgender Impulse ist. Die letzte Bedingung ist durch geeignete Wahl der Protonenprobe erfüllbar.

Die HF-Spannung wird gleichgerichtet, verstärkt und auf ein Zeigerinstrument gegeben, auf dem der Resonanzzustand alsodurch Zeigerausschlag angezeigt wird.

Als Frequenz-Normal diente der Langwellen-Sender Droitwich I auf 200 kHz, dessen Frequenzgenauigkeit mit $2 \cdot 10^{-8}$ angegeben wird. Dieser Sender kontrollierte einen 100 kHz-Quarzoszillator, der durch Frequenzvergleich mittels Lissajou'scher Figuren Eichpunkte auf der Skala eines variablen Meßsenders (BC 221) lieferte. Diese Eichpunkte lagen in unmittelbarer Nähe der zu messenden Resonanzfrequenzen. Deren Messung wurde ebenfalls mit Hilfe von Lissajou'schen Figuren auf einem Oszillographenschirm durchgeführt.

Der Sender Droitwich stellt ein Frequenznormal dar, das für unsere Messungen als fehlerfrei betrachtet werden kann. Lediglich durch die dreimalige Übertragung dieser Ausgangsfrequenz, nämlich vom Empfänger zum Quarzoszillator, vom Quarzoszillator zum Meßsender, vom Meßsender zum Resonanz-Detektor, ergeben sich Einstellfehler, die bei jeder Übertragung höchstens $1 \cdot 10^{-6}$ betragen. Der Gesamtfehler von $3 \cdot 10^{-6}$ braucht aber nicht gesondert in Rechnung gestellt zu werden, da er statistischer Natur ist und in der Streuung der Meßergebnisse mit erfaßt wurde.

Die Wahl der geeigneten Protonenprobe erfolgte nach dem Gesichtspunkt

eines optimalen Kompromisses. Während nämlich Proben mit kurzer Relaxationszeit die Resonanzkurve verbreitern und dadurch die Meßsicherheit der Resonanz beeinträchtigen, erschweren Proben mit langer Relaxationszeit die Einstellung der Resonanz dadurch, daß die Anzeige zeitlich der Einstellung nachschleppt. Als günstig erwies sich eine FeCl_3 -Lösung mit $T_1 = 0.6$ s und $10^{17} \text{ Fe}^{+++}/\text{cm}^3$.

Unsere zuletzt (1956) durchgeführten Messungen hatten das Ergebnis

$$\gamma' = (2.67549 \cdot 10^4) \text{ s}^{-1} \text{ G}^{-1} \text{ (diamagnetisch unkorrigiert)}.$$

Gegenüber unserem vorjährigen Ergebnis [1] liegt eine geringe Verschiebung vor, die auf eine Verbesserung in einigen Punkten der Versuchsanordnung zurückzuführen ist.

Der wahrscheinliche Fehler dieses Wertes beträgt $\pm 3 \cdot 10^{-5}$ und setzt sich aus folgenden Einzelfehlern zusammen:

Normalelement	$1 \cdot 10^{-5}$
Normalwiderstand	$1 \cdot 10^{-5}$
Spulendimensionen	$2 \cdot 10^{-5}$
Meßunsicherheit der Resonanz . . .	$2 \cdot 10^{-5}$

Das oben angeführte Ergebnis wurde ermittelt aus 16 Meßreihen zu je 20 Meßpunkten. Die Ergebnisse der Meßreihen sind im folgenden tabellarisch zusammengefaßt.

Meßreihe	f_1 (Hz)	f_2 (Hz)	f (Hz)	ω (s^{-1})	γ' ($\text{s}^{-1} \text{ G}^{-1}$)
1	436 632	432 900	434 766	2 731 715	$2.67548 \cdot 10^4$
2	638	916	777	784	555
3	632	911	772	753	552
4	632	926	779	797	556
5	676	863	769	734	550
6	632	874	753	634	540
7	638	911	775	772	554
8	632	905	769	734	550
9	621	895	758	665	543
10	643	905	774	766	553
11	632	895	763	697	546
12	627	895	761	684	545
13	632	905	769	734	550
14	638	895	767	722	549
15	632	890	761	684	545
16	638	879	759	671	544
					$2.67549 \cdot 10^4$

Infolge der Tatsache, daß durch die diamagnetische Wirkung der Elektronenhülle am Ort des Kernes nicht das gemessene äußere Feld H herrscht, ist am Ergebnis noch eine diamagnetische Korrektur anzubringen, die auf Grund theoretischer und experimenteller Untersuchungen $2.62 \cdot 10^{-5}$ beträgt. Damit nimmt unser Ergebnis den Wert

$$\gamma = (2.675\,56 \pm 0,000\,08) \cdot 10^4 \text{ s}^{-1} \text{ G}^{-1}$$

an.

Da es unwahrscheinlich ist, daß das gyromagnetische Verhältnis feldstärkeabhängig ist, ist für den Unterschied von $1 \cdot 10^{-4}$ zwischen unserem Ergebnis (2.675 49) und dem der amerikanischen Autoren (2.675 23) folgende Erklärung möglich:

Die Feldbestimmung erfolgte bei den amerikanischen Messungen mit einer Cotton-Waage, wobei gilt: $H = P/LI$ (P : Kraft auf den stromdurchflossenen Leiter, L : Länge des Leiters, I : Strom im Leiter). Es ergibt sich also

$$\gamma_1 = \omega/H = \omega \cdot L \cdot I/P = C' \cdot I_{\text{abs}}.$$

Bei unseren Messungen wurde das Feld durch Messung des Spulenstromes bestimmt, so daß das Feld $H = kI$ beträgt. (k : Spulenkonstante, I : Spulenstrom). Damit wird

$$\gamma_2 = \omega/H = \omega/K \cdot I = C''/I_{\text{abs}}.$$

Unter der Voraussetzung, daß beide Messungen frei von systematischen Fehlern sind, d.h.u.a., daß die Ströme I in internationalen Einheiten fehlerfrei bestimmt worden sind, läßt sich die Differenz zwischen γ_1 und γ_2 dadurch erklären, daß die z.Z. gültige Relation $1A_{\text{int}} = 0.999\,85A_{\text{abs}}$ mit einem Fehler behaftet ist. Mit einem q -Wert, der um die Hälfte der γ -Differenz erhöht ist, also mit

$$q = 0.999\,90$$

würden die beiden Messungen übereinstimmend

$$\gamma = 2.675\,43 \cdot 10^4 \text{ s}^{-1} \text{ G}^{-1} \text{ (diamagnetisch korrigiert)}$$

ergeben.

LITERATUR

- [1] F. KIRCHNER and W. WILHELMY: *Zei s. f. Na ur/or.*, **10a**, 657 (1955).

Die Massen der leichten Nuklide.

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1. – Gegenwärtiger Stand der Massenberechnungen aus den experimentellen Daten.

Die für die Berechnung von Nuklidenmassen in Betracht kommenden experimentellen Werte, die wir auch kurz als Q -Werte bezeichnen wollen, wurden in mustergültiger Weise in einer Reihe von Berichten im Oktober-Heft der *Review of Modern Physics*, 1954 zusammengestellt. Für die Berechnung der Massen der leichten Nuklide kommen die Daten in Frage, die in den Berichten von VAN PATER und WHALING [1] über die bei Kernreaktionen frei werdenden Energien, von KING [2] über totale β -Zerfallsenergien und von DUCKWORTH und Mitarb. [3] über massenspektrographische Dublettwerte gesammelt worden sind. Auf diese Berichte werden wir uns im Folgenden mit I, II und III beziehen. Für die Berechnung von Nuklidenmassen aus diesen experimentellen Daten ergab sich dabei folgende allgemein bekannte Situation: Das in den Berichten I und II gesammelte Material ist mit wenigen Ausnahmen in sich widerspruchsfrei und liefert einen bestimmten Satz von Massen. Etwas größere Massenwerte ergeben sich in der Regel, wenn man die in Bericht III zusammengestellten Messungen benutzt. Bei letzteren zeigen sich jedoch oft unerklärte Diskrepanzen zwischen den Werten verschiedener Autoren für das gleiche Dublett; selbst wenn es sich um Messungen des gleichen Autors unter verschiedenen Bedingungen handelt, zeigen sich oft Unstimmigkeiten, die beweisen, daß diese Messungen durch systematische Fehler entstellt sein müßen. In den letzten Jahren gelang es nun, eine Reihe von Ursachen für solche Fehlmessungen aufzudecken und auszumerzen. Insbesondere hat inzwischen Professor NIER die mit seinen Mitarbeitern [4] gemachten neuesten Messungen der leichten Massen bis ^{32}S publiziert, die in so glänzender Weise durch neue noch nicht veröffentlichte Messungen von L. G. SMITH [5] bestätigt werden

daß man den Eindruck gewinnt, daß hier ein in sich übereinstimmender Satz von massenspektroskopisch bestimmten Massen vorliegt. Diese Übereinstimmung der Meßergebnisse ist um so wertvoller, als sie bekanntlich mit ganz verschiedenen Methoden gewonnen wurde — in Minneapolis in dem neuen von NIER entwickelten großen doppelfokussierenden Massenspektrometer und in Brookhaven in dem neuartigen Massensynchrometer von SMITH. Diese Massen sind jedoch mit wenigen Ausnahmen um einen außerhalb der Fehlerangaben liegenden Betrag größer als die aus kernphysikalischen Daten berechneten Massen.

Es soll hier daran erinnert werden, daß sich schon bald nach den ersten genauen Massenbestimmungen durch ASTON eine ähnliche Lage ergeben hatte. Die Messungen von RUTHERFORD und OLIPHANT über die bei einigen Kernumwandlungen leichter Nuklide frei werdenden Energien hatten damals ASTON zu einer Revision seiner Massenmessungen gezwungen. So hat im Laufe der Zeit das Pendel einmal nach der einen und einmal nach der anderen Seite ausgeschwungen, wobei die Unstimmigkeiten entsprechend dem Fortschritt in der Genauigkeit der Methoden zwar immer kleiner wurden, aber eben doch öfters außerhalb der Fehler lagen. Nach der oben geschilderten Lage der Dinge sollte man heute, glaube ich, wieder einmal versuchen, ob nicht durch Änderung einiger kernphysikalischer Daten Übereinstimmung zu erzielen wäre. Dies soll im Folgenden versucht werden und mag vielleicht Anregungen zu neuen Messungen auf dem durch die Berichte I und II behandelten Gebiet geben. Zunächst soll aber die Durchführung einer Ausgleichsrechnung skizziert werden, die wir in unserem Institut gemeinsam mit L. WALDMANN, R. BIERI und F. EVERLING [6] durchgeführt haben und für die die experimentellen Daten der Berichte I und II zugrunde gelegt wurden.

2. – Zusammenhang zwischen den Q -Werten und den Massen bzw. den Bindungsenergien.

Für unsere Zwecke charakterisieren wir jedes Nuklid durch die Massen- oder Nukleonenzahl $A = N + Z$ und den Neutronenüberschuß $I = N - Z = 2T_z$ (T_z = Isotopenspin). Die Masse oder der Massenüberschuß M ist gegeben durch:

$$(1) \quad M(A; I) = \frac{1}{2}A(^1\text{n} + ^1\text{H}) - \frac{1}{2}I(^1\text{n} - ^1\text{H}) - E,$$

wobei E die Bindungsenergie der Nukleonen im Kern bedeutet. Wenn wir von den Messungen aus Mikrowellenspektren absehen, die im Gebiet der leichten Massen kaum eine Rolle spielen, so können wir sagen, daß alles, was wir über Massen wissen und experimentell messen können, Linearkombinationen sind, die die Eigenschaft haben, daß sich die Massenzahlen herausheben. Die Massen sind darin mit einfachen, ganzen oder gebrochenen Zahlen z

multipliziert, die wir in Analogie zu den chemischen Reaktionen als «stöchiometrische Koeffizienten» bezeichnen wollen. Eine solche Linearkombination der Massen wollen wir einen Q -Wert nennen. Es ist also:

$$(2) \quad \sum_i \kappa_i M_i = Q, \quad \text{wenn} \quad \sum_i \kappa_i A_i = 0.$$

Aber auch alle Größen, die man aus einem Satz miteinander in Übereinstimmung befindlicher Massen zu berechnen wünscht, sind solche Linearkombinationen der Massen, also Q -Werte im Sinne von Gl. (2). Dazu zählen z.B. die Bindungsenergien $E(N, Z)$, die Anlagerungsenergien des jeweils letzten Nukleons oder Nukleonenpaares sowie die Energiedifferenzen von zwei benachbarten Isobaren, die ungefähr den ersten Ableitungen der Energiefläche $E = E(N, Z)$ in Richtung von N und Z sowie von A entsprechen, die Paarungsenergien, die als zweite Ableitungen von E nach N bzw. Z aufgefaßt werden können u.a.m. Wegen der Korrelation, die demnach zwischen diesen Größen und den direkt gemessenen experimentellen Daten besteht, sind erstere auch oft mit viel größerer Genauigkeit bekannt als die Massen selbst.

Bei den experimentell gemessenen Q -Werten, die zur Berechnung der Massen herangezogen werden, unterscheidet man drei Arten:

1) Q_r -Werte, d.h. die bei Kernreaktionen frei werdenden Energien. Hier sind nur drei oder vier stöchiometrische Koeffizienten von Null verschieden und sie haben meist die Werte $+1$ oder -1 . Da bei Kernreaktionen keine Umwandlung von Neutronen in Protonen oder umgekehrt stattfindet, sich somit I insgesamt nicht ändert, ist immer, wie aus Gln. (1) und (2) folgt:

$$(3) \quad Q_r = - \sum_i \kappa_i E_i, \quad \text{da} \quad \sum_i \kappa_i I_i = \Delta I = 0.$$

Aus Q_r -Werten lassen sich also die Bindungsenergien sämtlicher, durch Kernreaktionen erfaßten Atomkerne berechnen. Für die Berechnung von Massen ist die Festlegung eines Standards, z.B. $^{16}\text{O} = 0$ notwendig. Das bedeutet nach Gl. (1), daß

$$(4) \quad ({}^1_0\text{n} + {}^1_1\text{H}) = \frac{1}{8}E(^{16}_8\text{O}).$$

Da Q_r -Werte keine Information über $({}^1_0\text{n} - {}^1_1\text{H})$ liefern, lassen sich aus ihnen nur die Massen von Nukliden mit $I = 0$ berechnen.

2) Q_β -Werte oder totale β -Zerfallsenergien. Hier reduziert sich die Linearkombination auf eine Differenz zwischen der Masse des Anfangs- und des Endkerns. Unter Q_{β_r} ist bereits wie üblich die um $2m_0$ vermehrte Zerfalls-

energie verstanden. Es ist also:

$$(5) \quad Q_{\beta^{\pm}} = M_a - M_e = \mp ({}^1\text{n} - {}^1\text{H}) - (E_a - E_e),$$

da $\Delta I = \mp 2$ für β^{\pm} -Zerfall.

Aus Q_{β} -Werten allein ergeben sich natürlich nur die Massen von Nukliden, die mit dem Standard isobar sind. Sie enthalten aber die wichtige Differenz $({}^1\text{n} - {}^1\text{H})$ und im Verein mit den Q_r -Werten lassen sich nun nach den Gln. (1) und (3) alle Massen berechnen. Das eben Gesagte gilt allerdings nur unter der bei solchen Massenberechnungen stets gemachten Annahme, daß die Ruhmasse m_ν des Neutrinos verschwindet. Zieht man zur Berechnung von Massen neben Q_r -Werten nur Q_{β} -Werte heran oder gehen die Q_{β} -Werte gegenüber den Q_{β^+} -Werten mit überragendem Gewicht ein, wie dies bei unserer Ausgleichsrechnung der Fall ist, dann wären, wie sich leicht zeigen läßt, alle Massen um $\frac{1}{2}Im_\nu$ zu erhöhen, wenn irgendwie durch andere Experimente ein von Null verschiedener Wert von m_ν festgestellt würde.

3) Q_m -Werte, unter welchen wir massenspektrographische Dublettwerte verstehen wollen. Für diese gilt:

$$(6) \quad Q_m = \frac{1}{2}({}^1\text{n} - {}^1\text{H})\Delta I - \sum_i \kappa_i E_i,$$

wobei ΔI verschiedene Werte annehmen kann. Aus ihnen allein ergeben sich zwar die Massen der stabilen und, soweit sie in einer für die Messung ausreichenden Menge erlangbar sind, auch der instabilen Nuklide mit Ausnahme von ${}^1\text{n}$. Daher können aus Q_m -Werten keine Bindungsenergien E berechnet werden. Erst durch Heranziehung mindestens eines oder mehrerer Q_r -Werte, die die in Gl. (6) auftretende $\sum \kappa_i E_i$ liefern, können $({}^1\text{n} - {}^1\text{H})$ und damit auch die Bindungsenergien der Kerne berechnet werden. Z.B. ist

$$(7) \quad ({}^1\text{n} - {}^1\text{H}) = E_d - ({}^1\text{H}_2 - {}^2\text{D}),$$

wobei die Bindungsenergie E_d des Deuterons durch den Q_r -Wert der Reaktion ${}^1\text{H}(\text{n}, \gamma){}^2\text{D}$ gegeben ist. Im Verein mit einem sehr genau bestimmten Q_{β} -Wert, z.B. ${}^3\text{T}(\beta^-){}^3\text{He}$ ergäbe der zugehörige Q_m -Wert (${}^3\text{T} - {}^3\text{He}$) auch die Masse des Neutrinos:

$$(8) \quad m_\nu = ({}^3\text{T} - {}^3\text{He}) - {}^3\text{T}(\beta^-){}^3\text{He}$$

oder eine obere Grenze dafür.

3. - Allgemeines zur Ausgleichsrechnung.

Im Gebiete der leichten Nuklide ist die Zahl N der experimentell gemessenen Werte mit ihren Fehlern ($Q_I \pm q_I$, $I = 1, 2, \dots, N$) sehr viel größer als die Zahl n der Massen (M_i , $i = 1, 2, \dots, n$), die mit ihren Fehlern daraus zu berechnen sind. Mit anderen Worten das Problem ist stark überbestimmt und somit eine typische Aufgabe der Ausgleichsrechnung, ähnlich der Berechnung der atomaren Konstanten, wie sie seit 1929 insbesondere von R.T. BIRGE, von DUMOND u.a. von Zeit zu Zeit in vorbildlichen Arbeiten [7] durchgeführt wurde. Die Aufstellung ausgeglichener Werte $Q_I^* \pm q_I^*$ hat so zu erfolgen, daß Widersprüche verschwinden, d.h. daß jede Rechenmöglichkeit zu denselben ausgeglichenen Massenüberschüssen $M_i^* \pm m_i^*$ führt und dabei die Verbesserung $v_I = Q_I - Q_I^*$ absolut umso kleiner ausfällt, je genauer Q_I gemessen d.h. je kleiner der Fehler q_I ist. Dies wird nach Gauß am besten durch die Forderung erfüllt:

$$(9) \quad \sum_I p_I v_I^2 = \text{Minimum}.$$

Hier sind noch für jeden Meßwert die Gewichte $p_I = q_I^{-2}$ eingeführt. Ich glaube, daß Physiker die Gauß'sche Methode u.a. aus folgendem einfachen Grunde allen anderen vorgeschlagenen Methoden vorziehen. In dem einfachen Falle, daß die Q_I Beobachtungen ein und derselben Größe darstellen ergibt die Gauß'sche Forderung [9] als ausgeglichenen oder plausibelsten Wert Q^* das gewichtete bzw. das arithmetische Mittel, je nachdem ob die Gewichte p_I der verschiedenen Beobachtungswerte Q_I voneinander verschieden oder einander alle gleich sind. Irgendwie fühlen wir, daß dies so sein sollte. Jede andere Methode würde nicht das Mittel einer Serie von Beobachtungswerten als den plausibelsten Wert liefern.

Wir haben nach Gl. (2) N Gleichungen

$$(10) \quad Q_I^* = \sum_i \kappa_{Ii} M_i^* \quad (i = 1, 2, \dots, n; I = 1, 2, \dots, N),$$

wo die κ_{Ii} bekannte Koeffizienten (die «stöchiometrischen Koeffizienten» der Kernreaktionen) sind. Die Gauß'sche Forderung [9] führt dann bekanntlich auf die n linearen Normalgleichungen (*):

$$(11) \quad \sum_k a_{ik} M_k^* = \lambda_i, \quad (i = 1, 2, \dots, n).$$

(*) Als Näherungswert für jede Masse ist hier der Einfachheit halber die Massenzahl A_k eigengeführt. Bei der tatsächlichen Durchführung der Rechnung wird man jedoch bessere Näherungswerte benutzen.

wo die Koeffizienten der unbekannten Massen

$$(12) \quad a_{ik} = \sum_I \nu_{Ii} \nu_{Ik} p_I$$

durch die Gewichte und die früher erwähnten stöchiometrischen Koeffizienten bestimmt sind, während die rechten Seiten der Gleichunge

$$(13) \quad \lambda_i = \sum_I \nu_{Ii} Q_I p_I$$

außerdem die für den Ausgleich verwendeten Beobachtungsdaten enthalten. Die Normalgleichungen [11] werden mit Hilfe der inversen Matrix (a_{ik}^{-1}) gelöst:

$$(14) \quad M_i^* = \sum_k a_{ik}^{-1} \lambda_k.$$

Die Matrix (a_{ik}^{-1}) gestattet aber zugleich auch die Angabe des ausgeglichenen Fehlers q^* irgend einer Linearkombination Q^* (im Sinne von Gl. (2)) der ausgeglichenen Massen M^* . Es ist

$$(15) \quad q^{*2} = \sum_{i,k} a_{ik}^{-1} \nu_i \nu_k \cdot$$

Speziell ist also der ausgeglichene Fehler der Massen M_i^* gegeben durch:

$$(16) \quad m_i^{*2} = a_{ii}^{-1}.$$

Leider ist es erst nach Durchführung der eben angedeuteten, in der Praxis sehr umfangreichen Rechnungen möglich, zu einem Test zu gelangen, der zeigt, ob man überhaupt berechtigt war, das vorgegebene Beobachtungsmaterial einem Ausgleich zu unterwerfen. Die Gauß'sche Methode verlangt nämlich, daß man zur Erteilung der Gewichte p_I die wahren Fehler der Beobachtungswerte benutzt und daß diese einer normalen (Gauß'schen) Verteilung genügen. Unter dieser Voraussetzung sollte das Minimum von Gl. (9) den Wert $N - n = r$ besitzen. In der Praxis stehen einem aber für die Erteilung der Gewichte p_I nur die von den Beobachtern angegebenen Fehler q_I zur Verfügung. Die Wurzel aus dem Verhältnis des tatsächlich erreichten Wertes des Minimums von Gl. (9) zu r ist als Verhältnis des Fehlers der Gewichtseinheit *nach* dem Ausgleich R_e (external consistency) zu demjenigen *vor* dem Ausgleich R_i (internal consistency) bekannt und man *erwartet* dafür den Wert 1 mit einem Fehler von $\pm (1/2r)^{\frac{1}{2}}$, d.h.

$$(17) \quad [\sum_I p_I v_I^2 / r]^{\frac{1}{2}} = R_e / R_i = 1 \pm (1/2r)^{\frac{1}{2}}.$$

Das gilt, wenn die Beobachter bei der Angabe der q_I mittlere und nicht wahrscheinliche Fehler gemeint haben. Im letzteren Falle ist die linke Seite von Gl. (17) mit $q_0\sqrt{2} = 0.6745\dots$ zu multiplizieren.

Bevor man mit den sehr umfangreichen Ausgleichsrechnungen beginnt, die sich nachher als wertlos oder ungerechtfertigt herausstellen könnten, wird man natürlich nach einem Verfahren suchen, das es einem ermöglicht, das dem Ausgleich zu unterwerfende Beobachtungsmaterial auf seine innere Übereinstimmung zu prüfen und somit die Spreu vom Weizen zu scheiden. Zu einem solchen Verfahren gelangt man mit Hilfe einer zweiten Methode zur Lösung der Gauß'schen Forderung (9), die ich hier nur soweit berühren will, als sie für das Verständnis des Folgenden wichtig ist. Anstatt nämlich sofort die Massen M_i^* zu berechnen, kann man auch zunächst nur die Beobachtungsdaten Q_I ausgleichen, ausgehend von der Bemerkung, daß zwischen diesen r linear unabhängige Bedingungen

$$(18) \quad \sum_I \alpha_{eI} Q_I^* = 0 \quad (e = 1, 2, \dots, r; r = N - n)$$

bestehen müssen, welche sich aus den Gln. (10) durch Elimination der M_i^* ergeben. Die experimentellen Werte Q_I werden die Gln. (18) nicht genau erfüllen, sondern die Residuen ε_e ergeben:

$$(19) \quad \sum_I \alpha_{eI} Q_I = \varepsilon_e.$$

Bei dieser Methode der Ausgleichsrechnung tritt eine Matrix (b_{ee}) auf, die unserer Matrix (a_{ik}) entspricht, von der uns aber hier nur die Glieder der Diagonale interessieren sollen. Sie sind durch

$$(20) \quad b_{ee} = \sum_I \alpha_{eI}^2 Q_I^2$$

gegeben, sodaß wir sagen können, wir erwarten, daß jede der Gln. (19) mit einem Fehler $\pm \sqrt{b_{ee}}$ erfüllt sein wird. Nun kann jede der Bedingungsgleichungen (19) einzeln durch ihr Verhältnis

$$(21) \quad R_e/R_t = l_e = \varepsilon_e/\sqrt{b_{ee}}$$

überprüft werden. Die Sichtung der Q -Werte, die als Eingangswerte für den Ausgleich aufgenommen werden sollen, erfolgt am besten durch Aufstellung der r Bedingungen (19) und die Beantwortung der Frage nach dem maximalen l_e -Wert, der noch zugelassen werden soll.

4. – Die Aufstellung des Systems der Reaktionszyklen.

Aus den Berichten I und II wurden für die Sichtung der experimentellen Daten die Q -Werte aller derjenigen Reaktionen und β -Zerfälle übernommen und in Abb. 1 eingezeichnet, durch die sich jede vorkommende Masse auf

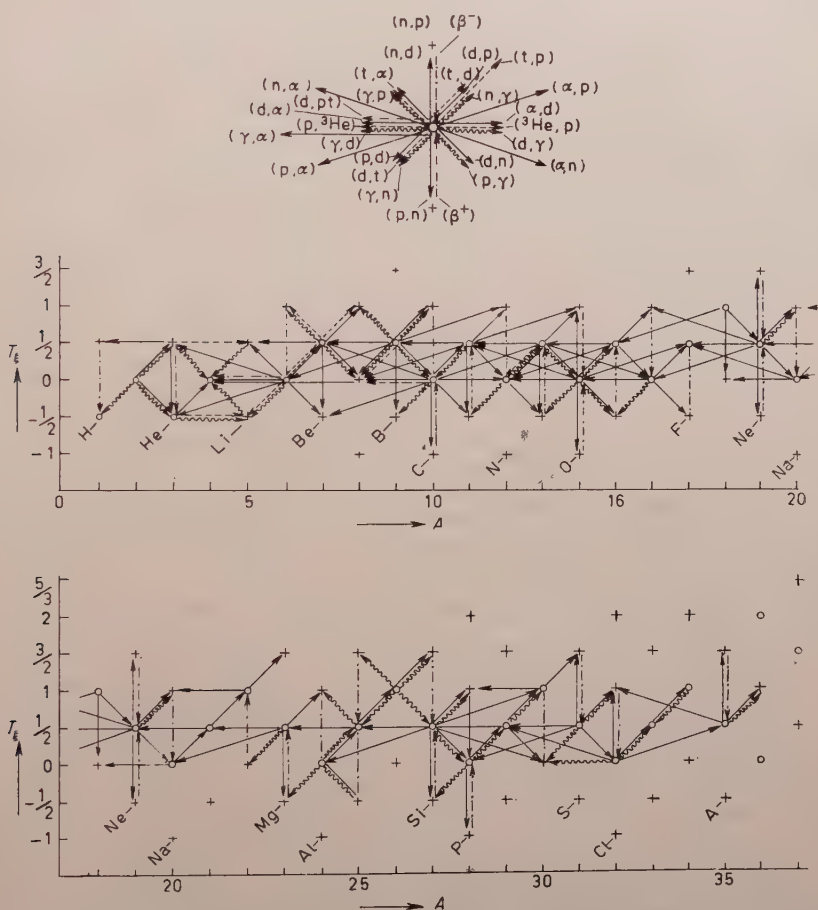


Abb. 1. - $A - T_\xi$ -Diagramm von ($n=70$) Nukliden mit ($N=196$) verbindenden Kernreaktionen und β -Zerfällen.

mindestens zwei verschiedenen Wegen berechnen läßt. Das bedeutet, daß jede Masse in mindestens zwei Q -Werten vorkommt oder daß in jedem Punkt von Abb. 1 mindestens zwei Pfeile beginnen oder enden. Werden keine Q_m -Werte für den Ausgleich benutzt, so kann man die Bedingungen (19) auf folgende Art leicht gewinnen. Umfährt man in Abb. 1 einen geschlossenen Polygonzug

und addiert die Q_r - und Q_β -Werte der aufeinander folgenden Reaktionen und β -Zerfälle mit dem richtigen Vorzeichen (positiv beim Fortschreiten in Richtung des Pfeiles und negativ beim Fortschreiten in entgegengesetzter Richtung), so heben sich die Bindungsenergien der die Ecken des Polygons bildenden Atomkerne auf; führt man als Hilfsgrößen bei den Kernreaktionen die Bindungsenergien der Geschoßteilchen E_d , E_t , E_τ und E_α bzw. bei den β -Zerfällen die Differenz (${}^1_0\text{n} - {}^1_1\text{H}$) ein und fügt sie der obigen Summe mit dem richtigen durch die Gln. (3) bzw. (5) gegebenen Vorzeichen hinzu, dann erhält man jeweils eine Linearkombination der Bedingungen (19). Tabelle I gibt eine Reihe von Beispielen solcher unter der Bezeichnung Zyklen bekannter Bedingungen. Die Prozesse bezeichnen dabei in einfach verständlicher Weise die hier einzusetzenden Werte Q_i ; hinzu kommen noch die in Tabelle II zusammengestellten Hilfsgrößen. Auf letztere sowie auf das bei der Aufstellung der Zyklen angewandte Verfahren kommen wir gleich zurück. Hier bemerken wir noch, daß die Koeffizienten α_{Q_i} außer für die Hilfsgrößen stets $+1$ oder -1 sind.

Nebenbei sei erwähnt, daß man auch aus Q_m -Werten leicht ähnliche Zyklen bilden kann und daß schließlich jeder Streckenzug in Abb. 1, der zwei massenspektroskopisch bestimmte Nuklide miteinander verbindet, eine Bedingung (19) ergeben würde, wenn man die vorkommenden Q_r -, Q_β - und Q_m -Werte gemäß den Gln. (3), (5) und (6) kombiniert und die Hilfsgrößen von Tabelle II entsprechend berücksichtigt. Die Aufstellung solcher Bedingungsgleichungen deckt die eingangs erwähnte Diskrepanz zwischen den Q_m -Werten untereinander und mit den Q_r - und Q_β -Werten auf und führt zu ihrer Ausscheidung für den von uns vorgenommenen Ausgleich.

Bei der Aufstellung der Zyklen (19) ist zunächst zu beachten, daß unter Polygonen auch die «Zweiecke», d.h. solche zwei Punkte in Abb. 1 verstanden werden müssen, die durch mehr als einen Pfeil miteinander verbunden sind. Führt man in der oben angegebenen Weise für die Dreiecke, Vierecke und höheren Polygone fort, so erhält man sehr leicht viel mehr als r Zyklen, d.h. sie sind nicht linear unabhängig voneinander und vor allem ist man alles andere als willkürfrei in der Auswahl der r linear unabhängigen Zyklen. Um diesen Nachteil zu beseitigen, fordern wir, daß die Zyklen so aufgestellt seien, daß jeder Zyklus den kleinstmöglichen Wert von b_{qq} besitzt, m.a.W. es soll in dem endgültig akzeptierten System (19) nicht möglich sein, durch einfache Addition und Subtraktion von Zyklen neue Zyklen mit kleinerem b_{qq} zu erhalten. Zur Illustration des oben gesagten diene Tabelle I. Hier sind zunächst 6 mit a bis f bezeichnete Zyklen aufgeführt, die sich unmittelbar aus Abb. 1 durch Umlaufen der entsprechenden Dreiecke ergeben. Zur Erleichterung des Folgenden ist unter jedem Prozeß der Fehler q_i des zugehörigen Q_i -Wertes in keV notiert. Nun sucht man durch fortlaufende additive und subtraktive Kombination dieser Gleichungen (wie in Spalte 1 von Tabelle I angegeben) solche Reaktionen oder Reaktionsgruppen zu eliminieren, die sich durch Reaktionsgruppen von

TABELLE I. — Zur Aufstellung des Systems der Zyklen. Prüfung von Q -Werten auf ihre Zuverlässigkeit mit Hilfe der Wert $l_q = \varepsilon_0 / \sqrt{b_{02}}$.

Nr. d. Nebenbed. q		Zur Aufstellung der Nebenbedingungen		$\varepsilon_0 \pm \sqrt{b_{02}}$ (MeV)	l_q
alt	neu				
a	(53)	$^{12}\text{C}(\text{d}, \text{n})^{13}\text{N} - ^{13}\text{C}(\text{p}, \text{n})^{13}\text{N} - ^{12}\text{C}(\text{d}, \text{p})^{13}\text{C}$		$\pm 0.000 \pm 0.005$	± 0.00
b	(54)	$^{13}\text{C}(\text{p}, \gamma)^{14}\text{N} - ^{14}\text{C}(\beta^-)^{14}\text{N} - ^{13}\text{C}(\text{d}, \text{p})^{14}\text{C}$	$+ (^{1}\text{n} - ^{1}\text{H}) - E_{\text{d}}$	$+ 0.078 \pm 0.080$	$+ 0.98$
c		$^{13}\text{C}(\alpha, \text{n})^{16}\text{O} + ^{16}\text{O}(\text{d}, \alpha)^{14}\text{N} - ^{13}\text{C}(\text{p}, \gamma)^{14}\text{N}$	$+ E_{\text{d}}$	$- 0.058 \pm 0.179$	$- 0.32$
d		$^{14}\text{N}(\gamma, \text{n})^{13}\text{N} - ^{12}\text{C}(\text{d}, \text{n})^{12}\text{N} - ^{14}\text{N}(\text{d}, \alpha)^{12}\text{C}$	$+ (E_{\alpha} - 2E_{\text{d}})$	$+ 0.030 \pm 0.215$	$+ 0.14$
e	(65)	$^{14}\text{N}(\text{d}, \alpha)^{12}\text{C} - ^{15}\text{N}(\text{p}, \alpha)^{12}\text{C} - ^{14}\text{N}(\text{d}, \text{p})^{15}\text{N}$		$- 0.185 \pm 0.080$	$- 2.30$
f		$^{14}\text{N}(\gamma, \text{n})^{13}\text{N} - ^{13}\text{C}(\text{p}, \text{n})^{13}\text{N} + ^{13}\text{C}(\text{p}, \gamma)^{14}\text{N}$		$- 0.077 \pm 0.215$	$- 0.36$
$b + c$	(57)	$^{12}\text{C}(\alpha, \text{n})^{16}\text{O} + ^{16}\text{O}(\text{d}, \alpha)^{14}\text{N} - ^{14}\text{C}(\beta^-)^{14}\text{N} - ^{13}\text{C}(\text{d}, \text{p})^{14}\text{C}$	$(^1\text{n} - ^1\text{H})$	$+ 0.020 \pm 0.160$	$+ 0.13$
$f - b$	(59)	$^{14}\text{N}(\gamma, \text{n})^{13}\text{N} - ^{13}\text{C}(\text{p}, \text{n})^{13}\text{N} + ^{13}\text{C}(\text{d}, \text{p})^{14}\text{C} + ^{14}\text{C}(\beta^-)^{14}\text{N}$	$- (^1\text{n} - ^1\text{H}) + E_{\text{d}}$	$- 0.155 \pm 0.200$	$- 0.7$
$f - b - d$		$^{14}\text{N}(\text{d}, \alpha)^{12}\text{C} + ^{12}\text{C}(\text{d}, \text{n})^{13}\text{N} - ^{13}\text{C}(\text{p}, \text{n})^{13}\text{N} + ^{13}\text{C}(\text{d}, \text{p})^{14}\text{C} + [(^1\text{n} - ^1\text{H}) - (E_{\alpha} - 3E_{\text{d}})]$		$- 0.185 \pm 0.081$	$- 2.28$
$f - b - d - a$		$^{14}\text{N}(\text{d}, \alpha)^{12}\text{C} + ^{12}\text{C}(\text{d}, \text{p})^{13}\text{C} + ^{13}\text{C}(\text{d}, \text{p})^{14}\text{C} + ^{14}\text{C}(\beta^-)^{14}\text{N}$	$- [(^1\text{n} - ^1\text{H}) + (E_{\alpha} - 3E_{\text{d}})]$	$- 0.185 \pm 0.081$	$- 2.28$
$f - b - d - a - e$	(X)	$^{14}\text{N}(\text{d}, \text{p})^{15}\text{N} + ^{15}\text{N}(\text{p}, \alpha)^{12}\text{C} + ^{12}\text{C}(\text{d}, \text{p})^{13}\text{C} + ^{13}\text{C}(\text{d}, \text{p})^{14}\text{C} + ^{14}\text{C}(\beta^-)^{14}\text{N} - [(^1\text{n} - ^1\text{H}) + (E_{\alpha} - 3E_{\text{d}})]$			
g	(97)	$^{26}\text{Mg}(\text{p}, \gamma)^{27}\text{Al} - ^{27}\text{Mg}(\beta^-)^{27}\text{Al} - ^{26}\text{Mg}(\text{d}, \text{p})^{27}\text{Mg}$	$+ (^1\text{n} - ^1\text{H}) - E_{\text{d}}$	$+ 0.157 \pm 0.300$	$+ 0.52$
h		$^{26}\text{Mg}(\text{p}, \gamma)^{27}\text{Al} - ^{26}\text{Mg}(\text{d}, \text{n})^{27}\text{Al}$	$- E_{\text{d}}$	$+ 0.493 \pm 0.304$	$+ 1.62$
$g - h$	(130)	$^{26}\text{Mg}(\text{d}, \text{n})^{27}\text{Al} - ^{27}\text{Mg}(\beta^-)^{27}\text{Al} - ^{26}\text{Mg}(\text{d}, \text{p})^{27}\text{Mg}$	$+ (^1\text{n} - ^1\text{H})$	$- 0.336 \pm 0.051$	$- 6.61$

TABELLE II. — Die Hilfszyklen für die Neutron-Proton-Differenz und die Bindungsenergien der Geschossteilchen.

Hilfsgrößen	Hilfszyklen	ausgeglichen	
		gemessene	Werte
		MeV ± keV	MeV ± keV
$(^1\text{n} - ^1\text{H}) =$	$^3\text{T}(^3\text{He} - ^3\text{T}(p, n)^3\text{He})$	0.7821 ± 1.0	0.7814 ± 0.9
$E_d =$	$^1\text{H}(n, \gamma)^2\text{D} \} - ^1\text{H}(d, p)^2\text{D} \}$	2.227 ± 2	2.2262 ± 1.3
$(E_\tau - E_d) =$	$^9\text{Be}(p, \alpha)^6\text{Li} + ^6\text{Li}(p, \alpha)^3\text{He} \{ + ^3\text{He}(\alpha, \tau)^4\text{He} \} - ^8\text{Be}(\gamma, \alpha)^4\text{He} - ^9\text{Be}(p, d)^8\text{Be}$	5.4955 ± 3.3	5.4939 ± 2.0
$(E_\tau - E_t) =$	$^3\text{T}(p, n)^3\text{He} \{ + ^3\text{He}(t, \tau)^3\text{T} \}$	-0.764 ± 1	-0.7634 ± 0.9
$[(^1\text{n} - ^1\text{H}) + (E_\alpha - 3E_d)] =$	$^{14}\text{N}(d, p)^{15}_7 + ^{15}\text{N}(p, \alpha)^{12}\text{C} + ^{12}\text{C}(d, p)^{13}\text{C} + ^{13}\text{C}(d, p)^{14}\text{C} + ^{14}\text{C}(\beta^-)^{14}\text{N}$	22.394 ± 9	22.395 ± 6
$E_\tau =$	$^9\text{Be}(p, \alpha)^6\text{Li} + ^6\text{Li}(p, \alpha)^3\text{He} \{ + ^3\text{He}(\alpha, \tau)^4\text{He} \} - ^8\text{Be}(\gamma, \alpha)^4\text{He} - ^9\text{Be}(\gamma, n)^8\text{Be}$	7.7195 ± 3.7	7.7201 ± 2.6
$E_t =$	$^9\text{Be}(p, \alpha)^6\text{Li} + ^6\text{Li}(p, \alpha)^3\text{He} - ^3\text{T}(p, n)^3\text{He} \{ + ^3\text{T}(\alpha, t)^4\text{He} \} -$ $- ^8\text{Be}(\gamma, \alpha)^4\text{He} - ^9\text{Be}(\gamma, n)^8\text{Be}$	8.4835 ± 3.8	8.4835 ± 2.6
$(E_t - E_d) =$	$(E_\tau - E_d) - (E_\tau - E_t)$	6.2595 ± 3.4	6.2573 ± 1.9
$(E_\alpha - 3E_d) =$	$[(^1\text{n} - ^1\text{H}) + (E_\alpha - 3E_d)] - (^1\text{n} - ^1\text{H})$	21.612 ± 9	21.614 ± 6
$(E_\alpha - 2E_d) =$	$[(^1\text{n} - ^1\text{H}) + (E_\alpha - 3E_d)] - (^1\text{n} - ^1\text{H}) + E_d$	23.839 ± 9	23.840 ± 6
$E_\alpha =$	$[(^1\text{n} - ^1\text{H}) + (E_\alpha - 3E_d)] - (^1\text{n} - ^1\text{H}) + 3E_d$	28.293 ± 11	28.292 ± 6

kleinerer Fehlerquadratsumme b_{ee} ersetzen lassen. Die konsequente Durchführung dieses Verfahrens ergibt automatisch $r+5$ voneinander linear unabhängige Zyklen. Zyklen, die bei der ersten Aufstellung überschüssig, d.h. nicht linear unabhängig von den übrigen waren, reduzieren sich von selbst auf solche, die mit einem dieser $r+5$ Zyklen identisch sind. Daß gerade $r+5$ Zyklen erhalten werden, ist notwendig, da wir 5 Gleichungen zur Bestimmung der 5 eingeführten Hilfsgrößen E_d , E_t , E_τ , E_α und ($^1n - ^1H$) brauchen. Zu ihrer Berechnung werden diejenigen 5 Zyklen ausgewählt, die die 5 voneinander linear unabhängigen Kombinationen der Hilfsgrößen mit der kleinsten Fehlerquadratsumme liefern. Sie sind in Tabelle II zusammengestellt und aus ihnen weiter andere Kombinationen der Hilfsgrößen berechnet worden, wie sie in dem nunmehr endgültig verbliebenen System (19) von r Bedingungen vorkommen. Bei Polygonen, die in der Nähe des Ursprungs von Abb. 1 liegen, ist es manchmal aus formalen Gründen nützlich, Reaktionen hinzuzufügen, deren Q -Werte definitionsgemäß Null sind. Solche Reaktionen sind in Tabelle II durch geschweifte Einklammerung gemerkt. Auf diese Weise kann man sich immer leicht davon überzeugen, daß man es mit einem richtigen Zyklus zu tun hat.

Nunmehr werden in die r Bedingungen für die auftretenden Prozesse sowie für die Hilfsgrößen die zugehörigen Werte $Q_i \pm q_i$ eingesetzt und nach den Gln. (19), (20) und (21) für jeden Zyklus die Werte von ε_e , b_{ee} und l_e berechnet. Nicht selten ist mit einer Erniedrigung des Wertes von b_{ee} im neuen gegenüber dem alten Gleichungssystem eine merkliche Erhöhung des Wertes von l_e verbunden. Dies wird besonders augenfällig in dem im unteren Teil von Tabelle I aufgeführten Beispiel, wo anstelle des alten Zyklus h der neue $g = 130$ tritt. Eine Erniedrigung von $\sqrt{b_{ee}}$ auf etwa den 6-ten Teil läßt l_e von dem unverfänglichen Wert 1.62 auf den, wie wir sehen werden, unzulässig hohen Wert 6.61 ansteigen.

5. — Die Sichtung der experimentellen Daten.

Die Beantwortung der Frage nach dem größten Wert von l_e , der noch für den Ausgleich zugelassen werden soll, wird durch das Wahrscheinlichkeitsintegral gegeben. Das System der r Zyklen können wir mit r voneinander unabhängigen Beobachtungen ein und derselben Größe vergleichen, deren wahren Wert — nämlich null — wir kennen. Ebenso ist z.B. in der Geodäsie der wahre Wert der Winkelsumme eines Polygons schon vor der Messung bekannt. Nur müssen wir hier die Voraussetzung machen, daß jede der r Beobachtungen mit einer anderen Methode gemacht worden sei, deren Genauigkeitsmaß durch die Streueung $\sqrt{b_{ee}}$ bestimmt ist. Die ε_e sind in diesem Vergleich die wahren Fehler jeder einzelnen Beobachtung. Noch anschaulicher ist es an

eine Kompanie von r Soldaten, die verschieden gute Schützen sein sollen, zu denken. Jeden Soldaten lassen wir einen Schuß auf eine Zielscheibe abgeben und messen den Abstand ε_ρ des Einschußpunktes vom Zielpunkt der Scheibe.

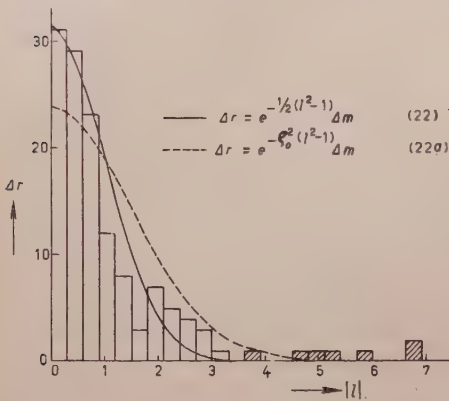


Abb. 2. - Verteilung der r Zyklenwerte $|l|$. Δr = Anzahl der Zyklen mit l -Werten zwischen $|l|$ und $|l| + 0.3$ (angezeigt durch die Höhe der Rechtecke), Δm = Anzahl der Zyklen mit l -Werten zwischen 0.85 und 1.15.

Die Streuung $\sqrt{b_{ee}}$ jedes Schützen sei aus vorhergehenden Schußserien bekannt. Zwischen den Werten l und $l + \Delta l$ werden die Schüsse von Δr Schützen (Zyklen) liegen. Ermitteln wir schließlich durch nachträgliches Abzählen die Anzahl Δm der Schützen (Zyklen), deren Schüsse im Intervall $(1 - \frac{1}{2}\Delta l) < l \leq (1 + \frac{1}{2}\Delta l)$ liegen, so liefert uns das Wahrscheinlichkeitsintegral die Verteilung der Schützen (Zyklen) auf die verschiedenen Werte von l . Diese Verteilung ist in Abb. 2 durch die ausgezogene (Gl. (22)) oder die gestrichelte Kurve (Gl. (22a)) gegeben, je nachdem man, zur Beurteilung der Genauigkeit der verwandten Methode bzw. der Güte der Schützen, die Streuung (mittlerer

Fehler der Einzelbeobachtung) oder den

wahrscheinlichen Fehler der Einzelbeobachtung (d.h. das $\rho_0\sqrt{2}$ -fache der Streuung) benutzt.

Nun wurde für jedes der aufeinanderfolgenden Intervalle der Größe $\Delta l = 0.3$ durch Abzählen die Anzahl der Zyklen ermittelt, die Werte von l_ρ in diesem Intervall haben. Die Anzahlen sind in dem Histogramm von Abb. 2 wie üblich durch die Höhe der Rechtecke wiedergegeben. Aus Abb. 2 muß man wohl schließen, daß die Verteilung der l_ρ -Werte, in der Mehrzahl der Fälle, besonders für $l_\rho < 2$, besser durch die ausgezogene Kurve (22) als durch die gestrichelte Kurve (22a) wiedergegeben wird, während für eine kleinere Zahl von Fällen, bei denen $l_\rho > 2$ ist, das umgekehrte der Fall zu sein scheint. Das bedeutet, daß die von den Beobachtern angegebenen und von uns zur Erteilung der Gewichte jeder Beobachtung verwendeten Fehlerangaben q_l im Durchschnitt als etwas aufzufassen sind, das zwischen dem mittleren und dem wahrscheinlichen Fehler liegt. Um den Ausgleich nicht unnötigerweise durch die Aufnahme von evtl. unrichtigen Meßwerten bzw. durch falsche Gewichtsverteilung zu fälschen, wurde daher beschlossen, als größten zulässigen l_ρ -Wert denjenigen im Intervall 3 bis 3.3 anzusehen, für dessen Auftreten Kurve (22) gerade noch eine merkliche von Null verschiedene Wahrscheinlichkeit angibt. Die 7 Zyklen mit l_ρ -Werten größer als 3.3 (in Abb. 2 sind die zugehörigen Rechtecke schraffiert) wurden aus dem System gestrichen und die nur in ihnen vorkommenden

9 Werte $Q_I + q_I$ nicht für den Ausgleich verwendet. Damit ergibt sich die Zahl der für den Ausgleich als Eingangswerte zugelassenen Werte Q_I zu $N = 196$, die $n = 70$ Massen enthalten und die durch $r = 126$ Zyklen miteinander verknüpft sind.

6. - Ergebnisse der Ausgleichsrechnung und Vergleich mit neuen massenspektroskopischen Messungen.

Wie in Abschnitt 4 erwähnt, ist für das Gauß'sche Minimum von Gl. (9) der Wert $r = 126$ zu erwarten. Tatsächlich erhielten wir den etwas höheren Wert $\sum_{I=1}^{196} p_I r_I^2 = 176.2$. Wie sich leicht zeigen läßt, entsprechen den Werten $p_I v_I^2$ in vielen Fällen die Werte l_o^2 der Bedingungen (19); das ist immer dann der Fall, wenn in einer Bedingungsgleichung (z.B. der q -ten) eines der Fehlerquadrate (das I -te d.h. q_I^2) stark die Summe aller übrigen in diesem Zyklus auftretenden Fehlerquadrate überwiegt. Es sei deshalb hier angemerkt, daß schon der in den beiden vorigen Abschnitten skizzierte Voraussgleich für die analoge Quadratsumme den ganz ähnlichen Wert $\sum_{q=1}^{126} l_o^2 = 166.5$ ergeben hatte. Für das wichtige Verhältnis R_o/R_i wäre nach Gl. (17) der Wert 1 ± 0.06 zu erwarten. Die Annahme, daß unter den q_I mittlere Fehler gemeint sind, liefert den etwas zu hohen Wert $R_o/R_i = 1.18$, während sich der etwas zu niedrige

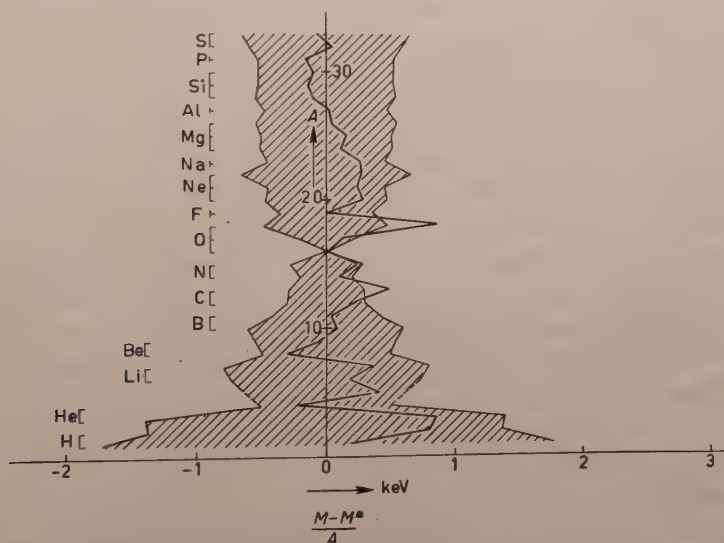


Abb. 3. - Vergleich von Massenwerten M , die von A. H. WAPSTRA berechnet wurden, zu den Massenwerten M^* des Ausgleichs aus kernphysikalischen Daten.

Wert $R_e/R_i = 0.80$ ergibt, wenn die q_i als *wahrscheinliche* Fehler aufzufassen sind. Daraus ist zu schließen, daß im Durchschnitt die Angaben der verschiedenen Autoren einem Fehler entsprechen, der zwischen dem mittleren und dem wahrscheinlichen Fehler liegt. Das ist vollkommen im Einklang mit dem, was wir bereits im vorigen Abschnitt aus dem Vorausbgleich, nämlich aus der Verteilung der l -Werte der $r = 126$ Zyklen (siehe Abb. 2) geschlossen hatten.

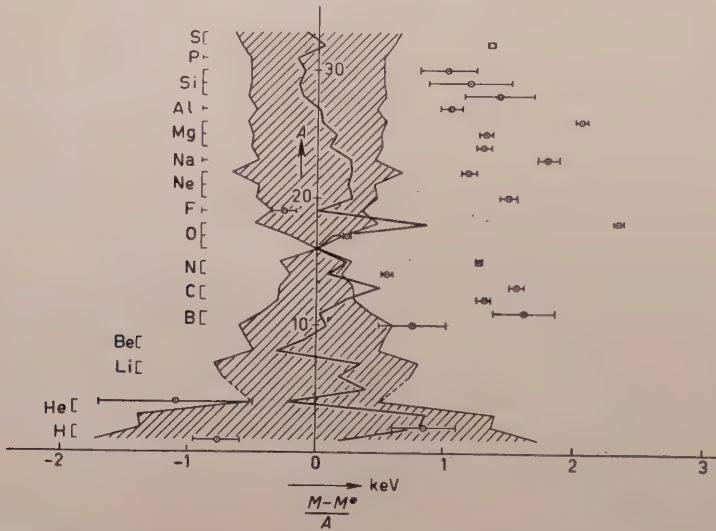


Abb. 4. – Vergleich der von A. O. NIER *et al.* und von L. G. SMITH massenspektroskopisch gemessenen Massen M mit den Massenwerten M^* des Ausgleichs aus kernphysikalischen Daten.

Einen Überblick über die Änderung der ausgeglichenen Fehler mit der Massenzahl A gibt das schraffierte Gebiet der Abb. 3, 4, 5 und 6, das das Fehlerintervall $\pm m^*/A$ des Packungsanteils M^*/A andeuten soll. Da die Fehler bei isobaren Nukliden oft sehr stark verschieden sind, wurde für die Zwecke der Abb. 3 bis 6 für jede Massenzahl das Nuklid mit dem kleinsten Fehler m^* gewählt. Es ist stets das stabile, was leicht verständlich ist, da dieses der Messung leichter zugänglich ist als die instabilen Isobare. Für $A = 8$, für das es kein stabiles Nuklid gibt, wurde ^8Be gewählt. Für $A = 5$ (^5He oder ^5Li) ist der Fehler so groß, daß er im Maßstab der Abbildungen nicht mehr eingetragen werden konnte.

Beginnend von ^{16}O , wo der Fehler des Packungsanteils definitionsgemäß gleich Null ist, steigt m^*/A mit fallendem A etwa proportional an, um bei ^1H den Wert ± 1.7 keV zu erreichen. Die Begrenzung des schraffierten Gebietes zeigt jedoch eine ausgesprochene Profilierung. Es fallen besonders die Ein-

schnürungen bei ^2D , ^4He und ^8Be auf. Die Massen der ersten beiden Nuklide sind durch zahlreiche genau gemessene (d, α) Reaktionen sehr gut bekannt.

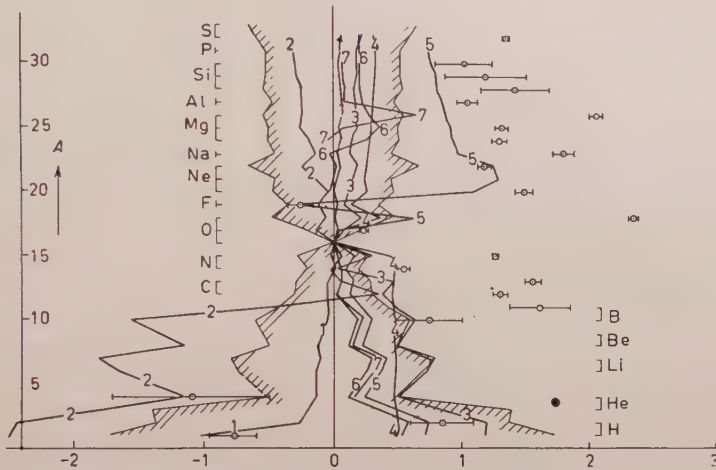


Abb. 5. – Massenänderungen ΔM^* , die durch eine Änderung ΔQ eines bestimmten, für den Ausgleich benutzten Q -Wertes hervorgerufen werden.

Kurve	Reaktion	ΔQ (keV)	Kurve	Reaktion	ΔQ (keV)
1	$^2\text{D}(\gamma, n) ^1\text{H}$	+ 4	5	$^{21}\text{Ne}(\text{d}, \alpha) ^{19}\text{F}$	+ 50
2	$^{10}\text{B}(\alpha, \text{d}) ^{12}\text{C}$	– 60	6	$^{25}\text{Mg}(\text{d}, \alpha) ^{23}\text{Na}$	+ 30
3	$^{13}\text{C}(\text{d}, \text{p}) ^{14}\text{C}$	+ 10	7	$^{27}\text{Mg}(\beta^-) ^{27}\text{Al}$	+ 40
4	$^{16}\text{O}(\text{d}, \alpha) ^{14}\text{N}$	– 7,5			

Aber auch zu ^8Be führen einige mit hoher Präzision gemessene Reaktionen und dieser Kern ist vor allem mit ^4He durch seinen sehr gut bekannten Zerfall in 2 α -Teilchen verbunden. Für Nuklide mit $A > 16$ etwa bis ^{32}S (auch hier könnte man die Profilierung näher begründen) erreicht m^*/A bald einen praktisch konstanten Wert, d.h. der hier allmählich wachsende Fehler der Q -Wertsmessung wird durch den Faktor $1/A$ ungefähr kompensiert.

Der stark ausgezogene Streckenzug in Abb. 3 zeigt den Unterschied zwischen den Massen M einer kürzlich von WAPSTRA [8] ausgeführten Massenberechnung und den Massen M^* unseres Ausgleichs. WAPSTRA zog für seine Berechnung ebenso wie wir nur Q_r - und Q_β -Werte heran. Doch beschränkt sich WAPSTRA auf etwa halb so viele Beobachtungsdaten wie wir, da er nur die mit größerer Genauigkeit gemessenen, bei denen der Fehler unter etwa 15 keV liegt, benutzt. Diese Daten werden außerdem auf gemeinsame Eichstandards um geringfügige Beträge korrigiert. Zwischen ^1n und ^{33}Cl werden die Massen von insgesamt 84 Nukliden berechnet. Ein vollständiger Ausgleich wurde dabei allerdings nur für die Massen von 15 Nukliden mit $A < 24$ vorgenommen. Wie man sieht, stimmen seine Massenwerte mit den unseren überall innerhalb der Fehler-

angaben überein. Auch bei ^{13}C und ^{18}O , die außerhalb des schraffierten Gebietes von Abb. 3 liegen, überdecken sich die beiderseitigen Fehlerintervalle. Die kleinen Unterschiede in den Massenwerten scheinen nicht so sehr in den oben erwähnten Unterschieden der Eingangswerte begründet zu sein, als vielmehr dadurch, daß WAPSTRA in dem Gebiet zwischen $A = 15$ und $A = 22$, das das schwächste Glied in der ganzen Kette der leichten Nuklide darstellt, einige neue Messungen von Q -Werten benutzt, die uns bei Beginn unserer Rechnung noch nicht zur Verfügung standen. Durch sie werden offenbar eine Reihe von Massenwerten um geringe Beträge erhöht. Diese Bemerkung scheint für das Folgende nicht unwesentlich zu sein.

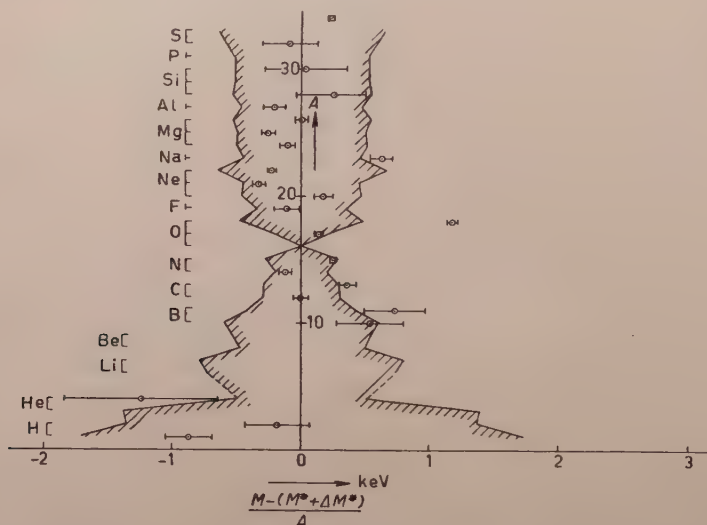


Abb. 6. – Vergleich zwischen den von A. O. NIER *et al.* und von L. G. SMITH massenspektrographisch gemessenen Massen M mit den geänderten Ausgleichsmassen $(M^* + \Delta M^*)$.

Für den Vergleich mit Massen aus Q_m -Werten, die im Folgenden mit $M \pm m$ bezeichnet seien, wurden die eingangs erwähnten Arbeiten von A. O. NIER *et al.* [4] und von L. G. SMITH [5] herangezogen. NIER *et al.* geben Werte von $M \pm m$ für alle stabilen Nuklide zwischen ^1H und ^{32}S an mit Ausnahme von ^4He , ^6Li , ^7Li und ^9Be , während wir aus Dublettmessungen, die uns freundlicherweise von L. G. SMITH brieflich mitgeteilt worden waren, die Massen $M \pm m$ von ^1H , ^2D , ^{10}B , ^{11}B , ^{12}C , ^{14}N , ^{32}S sowie von ^4He berechnen konnten. Die Unterschiede bei den in beiden Arbeiten gemessenen Nukliden sind so gering, daß sie im Maßstab der Abb. 4 nicht zum Ausdruck kommen würden, weshalb für sie gewichtete Mittelwerte gebildet wurden. Um die Übereinstimmung bzw. die Diskrepanz der massenspektroskopischen Werte M mit den

Massen M^* unseres Ausgleichs anschaulich zum Ausdruck zu bringen, wurden in Abb. 4 und 5 die Differenzen $(M - M^*)/A$ als kleine Kreise eingetragen. Die durch abgegrenzte Strecken angedeuteten Fehler sind die der massenspektroskopischen Messung, also m/A . An der Diskrepanz zwischen Massenwerten aus massenspektroskopischen Dubletts und aus kernphysikalischen Daten läßt sich nun nicht mehr zweifeln; die ersteren sind fast durchwegs größer, und zwar um Beträge, die meist außerhalb der Fehlerintervalle liegen. Die Abweichungen sind im großen und ganzen der Massenzahl A proportional mit einem Proportionalitätsfaktor von etwa 1.5 keV; doch überlagern sich dieser Proportionalität bei einzelnen Massen individuell verschiedene große Beträge. Da bei vielen der massenspektroskopisch gemessenen Nuklide $I = 0$ ist, kann man keinesfalls daran denken, die Diskrepanz dadurch zu beheben, daß man die Ausgleichswerte M^* durch Einführung einer von Null verschiedenen Neutrinomasse ändert. Auch ein Fehler im Umrechnungsfaktor zwischen mME und MeV kann nicht die Schuld tragen wie ein Vergleich der direkt gemessenen Q_m -Werte mit den entsprechenden Linearkombinationen Q^* aus dem Ausgleich lehrt. Angesichts der glänzenden Übereinstimmung der beiden massenspektroskopischen Arbeiten ist es auch schwer, sich eine Fehlerursache ausdenken, die diese Messungen in der angegebenen eigenartigen Weise verfälschen sollte. Es soll deshalb im Folgenden der Versuch unternommen werden, ob nicht durch Änderung einzelner kernphysikalischer Daten die Diskrepanz zu lösen ist.

Zunächst sieht man aus Gl. (1), daß eine Änderung der Differenz $(^1n - ^1H)$ nichts für die Verringerung der Diskrepanz beitragen kann, da I/A für alle hier in Betracht kommenden Nuklide mit Ausnahme von 1H entweder Null oder sehr klein ist. Eine Änderung von $(^1n + ^1H)$ dagegen würde die Proportionalität der Abweichung mit A erklären. Wie aus Gl. (4) hervorgeht, müßten dazu ein oder mehrere Q_r -Werte geändert werden, die zur Berechnung der Bindungsenergie von ^{16}O führen. Dabei ändern sich aber auch die Werte E von Gl. (1) in unübersichtlicher Weise und die Massenänderungen sind auf diese Weise nicht angebbar. Jedoch zeigt diese Überlegung, daß durch Änderung einzelner Q_r -Werte mehr zu erreichen wäre als durch Änderung von Q_β -Werten. Mit Hilfe der Matrix (a_{ik}^{-1}) lassen sich jedoch bei allen Massen M_i^* des Ausgleichs leicht die Beträge ΔM_i^* berechnen, um die sie sich ändern, wenn ein bestimmter Eingangswert — z.B. der I -te — um den Betrag ΔQ_I geändert wird. Aus Gl. (13) folgt zunächst, daß

$$(23) \quad \Delta \lambda_k = \kappa_{Ik} p_I \cdot \Delta Q_I,$$

da für diesen Fall die Summation über I entfällt. Das in Gl. (14) eingesetzt ergibt

$$(24) \quad \Delta M_i^* = p_I \Delta Q_I \sum_k \kappa_{ik} a_{ik}^{-1}.$$

Natürlich darf man nur den Meßwert Q_I und nicht den zugehörigen Fehler q_I und damit p_I ändern; denn das würde nach Gl. (12) eine Änderung der Matrix (a_{ik}) und somit auch von (a_{ik}^{-1}) bedeuten. Die Berechnung nach Gl. (24) ist sehr einfach, da die $\sum_k \kappa_{Ik} a_{ik}^{-1}$ lediglich die Summierung der in der gleichen

Zeile stehenden Glieder von 3 bis 4 Kolonnen der Matrix (a_{ik}^{-1}) mit den durch die stöchiometrischen Koeffizienten gegebenen Vorzeichen erfordert. Diese Summen sind dann noch mit dem konstanten Faktor $p_I \Delta Q_I$ zu multiplizieren, um die Änderungen sämtlicher Massen des Ausgleichs zu ergeben.

Um zu erfahren, bei welchen Q -Werten Änderungen am aussichtsreichsten sind und um welche Beträge ΔQ sie geändert werden sollten, wurden mit den massenspektroskopischen Werten $M \pm m$ die Q -Werte von möglichst vielen Prozessen berechnet und ebenso auch die Summe von Q -Werten aufeinander folgender Prozesse, die von einem massenspektroskopisch bestimmten Nuklid zum nächsten führen. Während sich in den meisten Fällen gute Übereinstimmung mit den Eingangswerten unseres Ausgleichs ergibt, zeigen sich bei einigen Prozessen, nämlich bei $^{10}\text{B}(\alpha, d)^{12}\text{C}$, $^{21}\text{Ne}(d, \alpha)^{19}\text{F}$ und $^{25}\text{Mg}(d, \alpha)^{23}\text{Na}$ Diskrepanzen ΔQ , die außerhalb der Fehlerangaben liegen. Ähnliche Fehlbeträge weisen die Summen $^{13}\text{C}(d, p)^{14}\text{C} + ^{14}\text{C}(\beta^-)^{14}\text{N}$ sowie $^{26}\text{Mg}(d, p)^{27}\text{Mg} + ^{27}\text{Mg}(\beta^-)^{27}\text{Al}$ auf, für die die Prozesse $^{13}\text{C}(d, p)^{14}\text{C}$ und $^{27}\text{Mg}(\beta^-)^{27}\text{Al}$ verantwortlich gemacht wurden. Die abgerundeten Fehlbeträge ΔQ sind in Abb. 5 unten bei jedem dieser Prozesse notiert. Die nach Gl. (24) berechneten Änderungen $\Delta M^*/A$ den jeder Fehlbetrag einzeln an den Massen des Ausgleichs hervorrufen würde, läßt sich anhand der numerierten Kurven in Abb. 5 leicht verfolgen. Man sieht z.B., daß die Änderung des Q -Wertes von $^{21}\text{Ne}(d, \alpha)^{19}\text{F}$ alle Massen oberhalb ^{16}O im richtigen Sinne um merkbare Beträge verschiebt, daß die Änderung des Q -Wertes von $^{13}\text{C}(d, p)^{14}\text{C}$ besonders für die leichten Massen eine ähnliche Wirkung hat, daß dagegen die Änderung der Q -Werte von $^{25}\text{Mg}(d, \alpha)^{23}\text{Na}$ und von $^{27}\text{Mg}(\beta^-)^{27}\text{Al}$ einen auf wenige Massen beschränkten Einfluß haben, und daß schließlich die Änderung des Q -Wertes von $^{10}\text{B}(\alpha, d)^{12}\text{C}$ fast alle ausgeglichenen Massen mit Ausnahme von ^{12}C verkleinert. Alle diese Massenänderungen addiert würden jedoch eine starke Diskrepanz bei ^1H hervorrufen. Es wurde daher auch der Q -Wert von $^2\text{D}(\gamma, n)^1\text{H}$ um denjenigen Betrag geändert, der nach Gl. (7) von der Differenz ($^1\text{n} - ^1\text{H}$) und dem massenspektroskopischen Dublett ($^1\text{H}_2 - ^2\text{D}$) verlangt wird. Um schließlich die Übereinstimmung mit den massenspektroskopischen Messungen, insbesondere bei den Nukliden unterhalb ^{16}O zu verbessern, wurde schließlich noch am Q -Wert der Schlüsselreaktion $^{16}\text{O}(d, \alpha)^{14}\text{N}$ eine Änderung ΔQ angebracht, die dem dreifachen Wert des für diese Reaktion angegebenen Fehlers entspricht. Wenn der Wert von ^4He von L. G. SMITH richtig ist, liegt dafür allerdings keine Berechtigung vor; ist er jedoch zu tief gemessen, was nicht unwahrscheinlich ist, dann wäre tatsächlich der Q -Wert der obigen Schlüsselreaktion zu erniedrigen, um mit den massen-

spektroskopischen Massen in Übereinstimmung zu kommen. Immerhin mag diese eine Änderung hier auch anstelle zahlreicher kleiner Änderungen stehen, die möglicherweise durch eine Summation von Fehlern entstanden sind.

Summiert man alle Massenänderungen, die durch die 7 hier vorgeschlagenen Änderungen ΔQ hervorgerufen werden, so erhält man einen neuen Satz von ausgeglichenen Massen ($M^* + \Delta M^*$). Mit diesen steht das Gros der massenspektroskopischen Massen M , wie aus Abb. 6 zu sehen ist, in ausgezeichneter Übereinstimmung. Es ist durchaus denkbar, daß die wenigen noch herausfallenden Werte, vor allem ^{18}O , durch Änderungen ΔQ an einer oder zwei noch unversuchten Reaktionen in Übereinstimmung gebracht werden können. Nur bei ^4He scheint es, als ob der Wert von L. SMITH um etwa 5 keV zu tief gemessen worden sei; doch berühren sich die beiderseitigen Fehlerintervalle.

Man kann noch fragen, ob durch die hier vorgebrachten Änderungen ΔQ das nach Gl. (17) berechnete Verhältnis R_e/R_i verschlechtert wird. Die umständliche Berechnung von $\sum_i p_i r_i^2$ wurde noch nicht durchgeführt. Doch kann gesagt werden, daß die entsprechende viel einfacher zu berechnende $\sum_e l_e^2$ um 3.2 kleiner wird, was bedeutet, daß die Übereinstimmung der Zyklen sich um eine Kleinigkeit verbessert hat. Im übrigen soll abschließend betont werden, daß mit diesen Ausführungen nur gezeigt werden sollte, daß es möglich ist, die massenspektroskopischen Messungen in Übereinstimmung mit den kernphysikalischen Daten zu bringen, wenn sich einige der letzteren um Beträge ΔQ , die etwa das dreifache des angegebenen Fehlers betragen, als falsch erweisen würden. Es müssen aber nicht unbedingt gerade die oben vorgeschlagenen Prozesse sein.

LITERATUR

- [1] D. M. VAN PATTTER und W. WHALING: *Rev. Mod. Phys.*, **26**, 402 (1954).
- [2] R. W. KING: *Rev. Mod. Phys.*, **26**, 327 (1954).
- [3] H. E. DUCKWORTH, B. G. HOGG und E. M. PENNINGTON: *Rev. Mod. Phys.*, **26**, 463 (1954).
- [4] K. S. QUISENBERRY, T. T. SCOLMAN und A. O. NIER: *Phys. Rev.*, **102**, 1071 (1956)
T. T. SCOLMAN, K. S. QUISENBERRY und A. O. NIER: *Phys. Rev.*, **102**, 1076 (1956).
- [5] L. G. SMITH: briefliche Mitteilung.
- [6] J. MATTAUCH, L. WALDMANN, R. BIERI und F. EVERLING: *Zeits. f. Naturfor.*, **11a**, 525 (1956).
- [7] Siehe J. W. M. DUMOND und E. R. COHEN: *Rev. Mod. Phys.*, **25**, 691 (1953).
- [8] A. H. WAPSTRA: *Physica*, **21**, 367 (1955).

Adjustment of Double - focusing Mass Spectrographs.

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The exactitude of the mass spectrographic nuclear mass determination depends greatly upon the sharpness of the edges of the lines. The sharper a line is the better it defines its position. The same is true of the steepness of the peaks which are measured with the mass spectrometers. For the best possible sharpness of line one must adjust with the greatest care. Good focusing also is essential in order to avoid systematic errors as was recently shown in collaboration with MATTAUCH [1].

It is easier to adjust a mass spectrometer than a mass spectrograph because one can see the peaks on the screen while adjusting and therefore we are concerned only with the mass spectrographs.

Only brief remarks have as yet been published about the adjusting of these machines. However BIERI [2] gave a systematic collection of the used quantities for intensity adjustment and sharpness adjustment and a description of the former technique in a dissertation.

We came upon this theory while experimenting with a MATTAUCH-HERZOG [3] mass spectrograph.

Since intensity adjustment presents no problem we shall immediately take up sharpness adjustment.

Adjustment eliminates inaccuracies of production and assemblage in some cases and compensates for them in other cases. It also reduces inaccuracies in the theory of focusing such as terms of higher order, therefore one obtains other values rather than the theoretical ones.

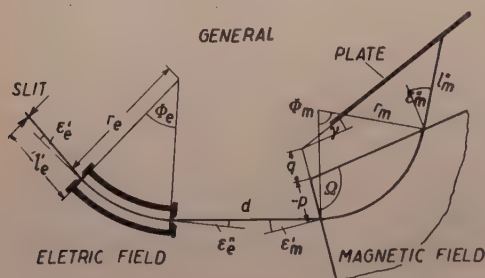


Fig. 1.

In order to make complete adjustment possible all concerned quantities must be ascertained. We do this for mass spectrographs which fulfill the following suppositions (Fig. 1).

The electric field is a sector of cylindrical condenser. One shoots almost vertically through the center of an electric field. The magnetic field is homogeneous and has the form of a sector. The plate is flat. The whole lense system is cylindrical, after the slit and fields have been brought in alignment by turn adjustment. Fig. 1 shows all quantities which define the position of the slit and fields of any mass spectrograph.

- l'_e is the distance of the slit from the electric field;
 ε'_e the angle at which the middle beam is shot in;
 ε''_e the angle of exit;
 r_e the middle radius on the condenser;
 Φ_e the angle of the sector;
 d the distance between the fields;
 ε'_m and ε''_m the angles of entrance and exit in the magnetic field;
 p the distance of the intersection of the edges of the field from the point of entrance;
 q the distance of the same point from the intersection which would be formed by the lines of the plate and the front edge of the field if they were longer;
 Φ_m the deflection angle in the magnetic field;
 Ω the angle of the sector of the magnetic field;
 γ the angle of the plate against the back edge of the field;
 l''_m the space of the beam from the magnetic field to the plate;
 r_m is the radius in the magnetic field.

Between these 15 quantities there are 4 geometrical connections, so that the geometry of the beam is fixed by exactly 11 quantities. The 4 equations are:

$$\begin{aligned}
 \varepsilon''_e &= \varepsilon'_e, & \Phi_m &= \Omega + \varepsilon'_m + \varepsilon''_m, \\
 p \sin \Omega &= -2r_m \sin \frac{\Phi_m}{2} \cos \left(\frac{\Phi_m}{2} - \varepsilon''_m \right), \\
 l''_m &= \frac{-\cos \left(\frac{\Phi_m}{2} - \varepsilon''_m + \gamma \right) \left[2r_m \sin \frac{\Phi_m}{2} + \frac{(q-p) \cos (\varepsilon''_m + \Omega)}{\sin (\Phi_m/2)} \right]}{\cos (\varepsilon''_m - \gamma)} + \\
 &\quad + \frac{(q-p) \cos ((\Phi_m/2) - \varepsilon''_m - \Omega)}{\sin \Phi_m/2}.
 \end{aligned}$$

If one changes for example the angle of entrance ε'_e , the angle of exit ε''_e is altered to the same degree.

Let's take these 11 geometrical independent quantities: l'_e , ε'_e , r_e , Φ_e , d , ε'_m , p , q , γ , Ω , r_m .

r_m must remain independent in order to get double focusing along the whole plate. If the M-H theory is generalized with regard to ε'_e , p and q , the double focusing condition has the following form:

$$[l'_e - g_e(r_e, \Phi_e, \varepsilon'_e)] \cdot \left[d - \frac{r_m^2 \left(\frac{\cos \varepsilon'_m \cos \varepsilon''_m}{\sin \Omega} \right)^2}{l''_m - \frac{\cos \varepsilon''_m \cos (\Phi_m - \varepsilon'_m)}{\sin \Omega}} - v_m \frac{\cos \varepsilon'_m \cos (\Phi_m - \varepsilon''_m)}{\sin \Omega} - g_e(r_e, \Phi_e, \varepsilon'_e) \right] = f_e^2(r_e, \Phi_e, \varepsilon'_e),$$

$$K''_{e1}(r_e, \Phi_e, \varepsilon'_e) + (d - l'_m)K''_{e2}(\Phi_e, \varepsilon'_e) = r_m(1 - \cos \Phi_m) + l'_m[\sin \Phi_m + (1 - \cos \Phi_m) \operatorname{tg} \varepsilon'_m].$$

$$\varepsilon'_e \ll 1, \quad p \text{ and } q \text{ arbitrary.}$$

In this equation

g_e means the distance of the focus from the electric field and

f_e the focal length of the electric field;

$K''_e = K''_{e1} + l'_e K''_{e2}$ is the velocity dispersion of the electric field;

l'_m is the distance between the intermediate image and the magnetic field.

The first equation shows the direction focusing, the second velocity focusing. MATTAUCH and HERZOG [3] showed that beams of equal energy must run parallel between the fields if double focusing along the plate is required; that means the slit must coincide with the forward point of focusing. They chose the specially practical case with vertical beam entrance into the magnetic field, the plate lies just behind the magnetic field (Fig. 2).

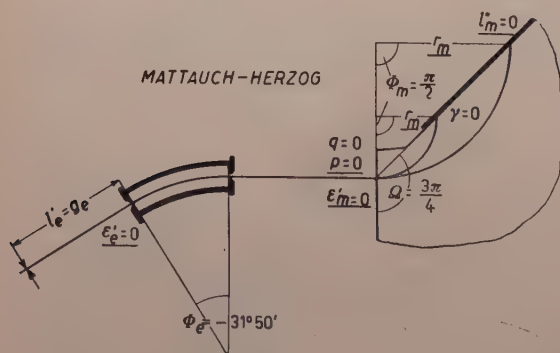


Fig. 2.

Now we can assume that the inaccuracies of the 10 quantities are small in the first order. That is, the relative inaccuracies are as large as the angle of aperture, which is chosen as about 10^{-3} . The question is, whether double focusing can be achieved if the quantities have

such inaccuracies. The equations are for the sake of simplicity specialized for the surrounding area of the M-H type. The results of a long calculation are:

$$[l'_e - g_e(r_e, \Phi_e, \varepsilon'_e)] \cdot r_m^2 + f_e^2 \left[\varepsilon'_m + 2 \left(\gamma + \Omega - \frac{3\pi}{4} \right) \right] \cdot r_m + f_e^2 (q - p) = 0,$$

$$\frac{r_e}{l'_m} \left(1 - \frac{1}{2} \sqrt{2} \right) + \left(\frac{d}{l'_m} - 1 \right) K''_{e2}(\Phi_e, \varepsilon'_e) = \frac{r_m}{l'_m} + 1 + \varepsilon'_m.$$

Double focusing condition for all masses:

$$\begin{aligned} (1) \quad & l'_e - g_e(r_e, \Phi_e, \varepsilon'_e) = 0, \\ (2) \quad & \varepsilon'_m + 2 \left(\gamma + \Omega - \frac{3\pi}{4} \right) = 0, \\ (3) \quad & q - p = 0, \\ (4) \quad & -K''_{e2}(\Phi_e, \varepsilon'_e) = 1 + \varepsilon'_m. \end{aligned}$$

The independence of r_m demands $l'_e - g_e$ for direction focusing. That is the slit must be on the point of focus even when it deviates from the theoretical position, or in other words beams having equal energy must run parallel to each other even when p , q and ε'_e are not zero. Therefore since the terms with $1/l'_m$ are negligible one arrives at the fourth equation. According to equations (2) and (3) the plate must coincide with the focus line, that is what the first equation required for one point. q equal p means that the point of entrance in the magnetic field coincides with the intersection which would be formed by the lines of the plate and the front edge of the field if they were longer.

In order to get double focusing of the first order for all masses it is essential to adjust at least 4 quantities in order to obtain experimentally the values determined by these 4 equations. In consideration of certain rules of selection which stem from the fact that every quantity does not appear in each equation and due to technical viewpoints we choose

- l'_e the distance of the slit from the electric field;
- ε'_e the angle at which the middle beam is shot in;
- p the distance of the intersection of the edges of the field from the point of entrance;
- ε'_m the angle of entrance in the magnetic field.

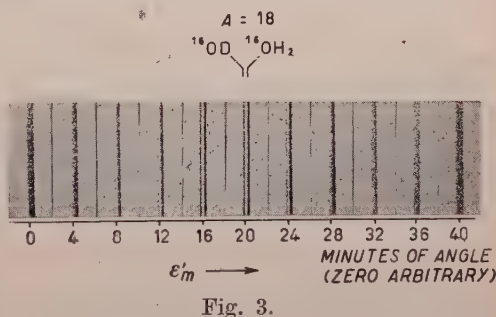


Fig. 3.

In reality it would suffice to alter one of these quantities in stages and to pick out the sharpest picture as shown in Fig. 3.

The three others remain constant. After iteration of the four quantities one arrives at the ultimate values. But this is inexact and inconvenient. Therefore we apply simultaneous double iteration as shown in Fig. 4.

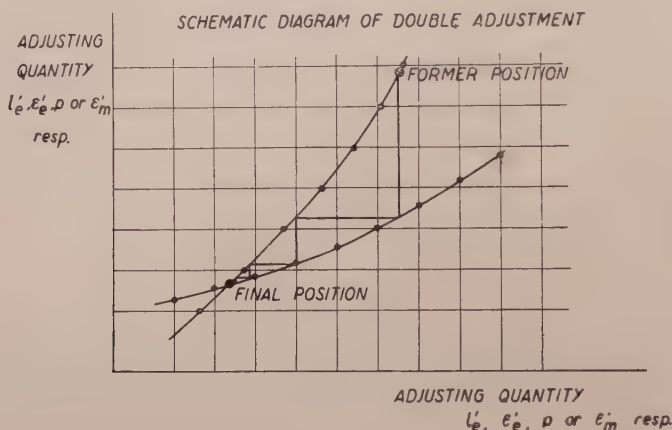


Fig. 4.

Here is given an illustration of single iteration for two quantities in which one must develop several plates. Instead of that we expose only one plate in all positions given by the intersections of the horizontal and vertical lines. And then in every horizontal and vertical line we seek the sharpest place. If one connects them one obtains two curves the intersection of which accurately determines the best values.

This diagram must be iterated with a second one which contains the other two quantities.

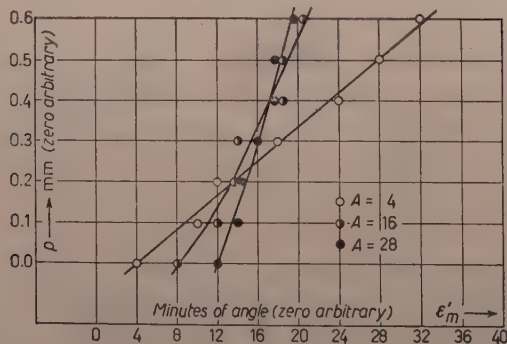


Fig. 5.

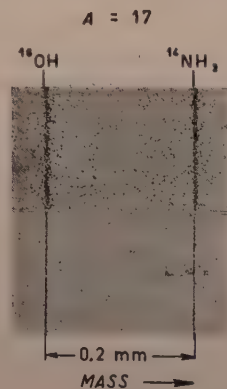


Fig. 6.

If one elects p and ε'_m for the simultaneous iteration both curves will always coincide. Then one only has to find the point of intersection of the different curves obtained by several masses (Fig. 5).

In the second diagram with l'_e and ε'_e which must be iterated with the first one the curves also coincide as shown by my coworker WENDE [4].

We are still working with this method of adjustment and so far it has been successful in every case. Fig. 6 shows a doublet to be measured.

The adjustment in this case was made with utmost care. The upper doublet was made by MATTAUCH and BIERI [5] before BIERI, MATTAUCH and ourselves [6] improved upon the machine. Adjustment was made with only three quantities in this case. The resolving power of the newer lines is M/dM 100 000.

* * *

The author is very grateful to professor Dr. J. MATTAUCH for many helpful discussion.

REFERENCES

- [1] F. EVERLING and J. MATTAUCH: *Zeits. f. Naturfor.*, **11a**, 68 (1956).
- [2] R. BIERI: *Dissertation* D77, University Mainz.
- [3] J. MATTAUCH and R. HERZOG: *Zeits. f. Phys.*, **39**, 786 (1934).
- [4] H. WENDE: private communication.
- [5] J. MATTAUCH and R. BIERI, private communication.
- [6] R. BIERI, F. EVERLING and J. MATTAUCH: *Zeits. f. Naturfor.*, **10a**, 659 (1955).

Il problema della scala doppia dei pesi atomici e il rapporto della Commissione per i pesi atomici dell'Unione Internazionale di Chimica per l'anno 1954-1955.

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La pubblicazione della tabella 1955 dei pesi atomici è stata accompagnata da una relazione del Presidente della Commissione prof. E. WICHERS [1], il quale propone di considerare se non convenga scegliere il ^{19}F come base della scala chimica dei pesi atomici e invita a valutare se una tale scelta, sempre che non presentasse ostacoli insormontabili nel confronto con le masse di altre specie nucleari, non possa favorire la unificazione delle due scale.

Il problema si pone attualmente in termini ben più gravi che per il passato, perchè le due scale differiscono oggi per quasi tre parti su 10 000, mentre nel 1931 differivano solo di una o due parti su 10 000.

Inoltre è noto che la composizione isotopica dell'ossigeno di diversa provenienza è lievemente variabile; pertanto se la scala chimica è considerata come basata sull'ossigeno naturale senza qualificazione, essa differisce dalla scala fisica per un fattore che varia da 1.000268 a 1.000278.

Pertanto la Commissione assume a base della scala chimica dei pesi atomici un « ossigeno convenzionale » costituito da una miscela di isotopi dell'elemento, avente una massa media di 1.000275 volte la massa del ^{16}O .

Una tale definizione è sufficiente ad eliminare il difetto logico di una scala che ha una base di riferimento variabile. Nell'adottare tale emendamento formale, la Commissione ha suggerito che prima di rendere definitiva una tale scelta, fosse considerata di nuovo la possibilità di unificare le due scale.

Nel rendermi portavoce di un tale desiderio, e portare in discussione il problema, desidero prospettare alcuni elementi favorevoli e altri sfavorevoli alla proposta.

La scelta del ^{19}F come elemento di riferimento dovrebbe esser fatta ponendo eguale a 19.00 la massa dell'elemento che nella scala chimica è $18.999\,2 \pm 0.000\,2$.

L'adozione del valore esatto 19 porterebbe una variazione di tutti i valori legati alla scala chimica di circa 1 parte su 25000.

Nella scala fisica, la massa del F^{19} è 19.0044: fissare il valore a 19 comporterebbe una diminuzione di tutte le masse di circa 2 parti su 10000.

Tali variazioni sarebbero di gran lunga inferiori a quelle che deriverebbero se si adottassero quali elementi di riferimento secondo precedenti proposte, $^1\text{H} = 1$ oppure il $^4\text{He} = 4$.

Nel primo caso ($^1\text{H} = 1$), i dati relativi alle masse atomiche varierebbero di circa 8 parti per 1000 e le variazioni sarebbero considerevoli per gli elementi più pesanti; nel secondo caso ($^4\text{He} = 4$), i valori di entrambe le scale subirebbero una variazione di 1 parte su 1000.

Se si confrontano le masse atomiche della scala chimica (1953) con quelle calcolate da dati puramente fisici, come ha fatto NIER [2] si può constatare che le divergenze tra i valori confrontati sono essenzialmente dovute a quattro cause d'errore: fattore di conversione; accuratezza nelle misure della massa isotopica; accuratezza nella determinazione dell'abbondanza relativa degli isotopi; variazione naturale dei rapporti isotopici.

La scelta del ^{19}F come elemento di riferimento sarebbe logica e razionale, dato che non si conoscono isotopi naturali del fluoro.

Contro tali fattori positivi, sta il fatto negativo che non si dispone oggi di una *misura spettrografica diretta* della massa del fluoro: i valori disponibili sono ricavati indirettamente dall'energia delle reazioni di disintegrazione nucleare [3].

Dati relativi ad altri elementi, ottenuti con questo metodo, sono generalmente considerati favorevolmente.

Si tratta di sapere se i valori relativi alla massa del fluoro, di cui attualmente si dispone e ricavati con metodi indiretti, si possono oggi ritenere sufficienti per fare del fluoro l'elemento di riferimento per una scala unificata di pesi atomici.

RIFERIMENTI

[1] E. WICHERS: *Journ. Am. Chem. Soc.*, **78**, 3235 (1956).

[2] A. O. NIER: *Zeits. f. Elektrochem.*, **58**, 559 (1954).

[3] C. W. WAHLING, W. A. FOWLER e C. C. LAURITSEN: *Phys. Rev.*, **83**, 512 (1951).

INTERVENTI E DISCUSSIONI

— MATTAUCH:

Thanks to prof. CAGLIOTI for raising the question. He thinks, on the basis of his personal experience, that at the present stage of development of mass spectrographic techniques, the mass spectrographic determination of the fluorine mass is very difficult.

The available data of the mass of fluorine have been obtained by indirect methods and are not sufficiently reliable to make fluorine the reference element.

He suggests that, at least for the moment, the «conventional oxygen» mass, as adopted by the IUPAC Commission, be retained, and that this discussion should be continued within the Commission.

The Determination of Radioactive Decay Constants.

F. BROWN (*) and G. R. HALL

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1. - Introduction.

The decay, or disintegration constant λ for a radioactive species is defined by the equation

$$-\frac{dN}{dt} = N\lambda,$$

where N is the number of atoms of the species and $-dN/dt$ is the disintegration rate. Hence

$$\frac{N_t}{N_0} = \exp[-\lambda t],$$

where N_0 is the number of atoms present at any arbitrary zero time and N_t the number present at a time t measured from this zero. Therefore λ is related to the half life $t_{\frac{1}{2}}$ of the species by the expression

$$\lambda = \frac{\log_e 2}{t_{\frac{1}{2}}}.$$

For a study of the theory and systematics of radioactive decay rough determinations of λ are generally adequate but in experimental studies where radioactive species are involved an accurate knowledge of the various λ 's is usually essential.

In a discussion of the measurement of half lives it is convenient to divide radioactive species into three rather arbitrary groups:

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1) Those which are so short lived that it is impossible to make a series of measurements of dN/dt as a function of time by conventional counting methods. This group includes those decays, usually γ -ray transitions, which have half lives in the order of milli- or micro-seconds.

2) Those of moderate half life where the decay can be followed over several half lives i.e. periods of a few seconds to a few months.

3) Those of such long half life that no large change in dN/dt occurs in a reasonable time.

The dividing lines between these groups depends to some extent upon what equipment is available and upon how much time can be devoted to the measurement. For measurements in group 1 it is usual to use special electronic techniques such as the method of delayed coincidence, although valuable information may often be obtained from recoil experiments or photographic plate studies. We do not propose to discuss these in this paper but to confine ourselves to surveying the methods which are applicable for measuring half lives which fall into groups 2 and 3. The latter presents special problems which are dealt with at some length.

2. - Measurements of moderate half lives.

The essence of measuring half lives of moderate duration is to obtain a decay curve, i.e. a plot of $\log dN/dt$ versus t , which should be a straight line if only one radioactive species is involved. The data are usually treated graphically but there are also standard methods of computing the decay constant and its statistical error [1]. The straightness of the decay curve is one of the most important criteria in assessing the worth of the measurement for it indicates the radiochemical purity or otherwise of the material, and also, when applicable, the presence or absence of « dead time » losses in the counting system. The longer the decay curve the more accurate is the resulting value for λ likely to be and the greater the certainty of radiochemical purity.

It is therefore an advantage to use a counting device which can accept a high counting rate and is yet sensitive for low counting rates. Thus proportional type β counters are preferable to Geiger counters. A typical proportional β counter having a « dead time » of 2 μ s will accept a counting rate at the beginning of the experiment of 10^4 s^{-1} with a loss of 2% (for which a correction can be made). If the background is 0.5 s^{-1} a counting rate of 5 s^{-1} is acceptable at the end of the decay and thus the decay can be followed for 10 half lives without changing the source or the counter geometry. Scintillation counters

using photomultiplier detectors will also accept high counting rates. The use of high counting rates also brings an improvement in the statistical accuracy of the data, an important point when the half life is small and long counting periods are not possible.

Stability of counting devices and sources over the duration of the experiments is essential. Proportional counters, ionization chambers and electroscopes can be made to have good long term stability whereas Geiger counters and scintillation counters are generally less satisfactory in this respect. The use of standard sources is valuable in ensuring counter stability especially if the standard emits radiations which are closely similar to those from the nuclide under study. The stability of the source is partly a matter of ensuring reproducible geometry in cases where the source must be removed and replaced periodically. This is most easily arranged when the counter has either 4π geometry or has very low geometry. Secondly it is necessary to avoid chemical changes in the source, absorption of moisture and mechanical disruption. Here again a decay curve with an adequate number of points of good statistical accuracy will show up lack of stability in counter or source.

The measurement of times—both the duration of the counts and the times at which they were made—can generally be done with sufficient accuracy without special precautions. Short times (in the order of a few seconds) can be measured conveniently by actuating a scaler which is recording a fixed frequency such as a 60 cycle per second A.C. main supply. For short half lives (less than a few minutes) some form of automatic equipment is needed. Thus electroscopes can be modified to work automatically [2], counting rates can be recorded in various ways on moving charts or strips of paper and scalers in which the counts are displayed in illuminated form can be photographed with cine-cameras.

Many instances occur in which the nuclide being studied cannot be obtained in a radio-chemically pure state. Radioactive isotopes may be present and radioactive daughters may also grow in during the measurements. The resulting decay curves are usually resolved into their components by graphical methods. In some cases a great advance can be made by using a sodium iodide crystal and photomultiplier (for γ -rays), an ionization chamber (for α -particles) or a xenon filled proportional counter (for X-rays and soft γ -rays), each in conjunction with some form of pulse height analyser. In these ways only radiation from the desired nuclide is accepted. As examples we can cite the measurement of the half life of ^{135}Xe present in a mixture of rare gas fission products by use of a γ -ray crystal spectrometer [3], the application of α pulse height analysis in measurements on the very heavy elements [4], and the determination of the half life of ^{241}Pu by studying the growth of its daughter ^{241}Am in a xenon filled proportional counter arranged to count the 60 keV γ -ray of ^{241}Am [5].

3. - Measurement of long half lives.

In some cases at least, long half lives can be measured by direct observation of the decay but, obviously, very accurate measurements are required when the change in N and dN/dt with time is small. Ionization chambers and electroscopes have generally been chosen for such measurements because they can be made to have good stability, are readily calibrated and ionization currents can in principle, at least, be measured with considerable accuracy. Various forms of balanced ion chambers have been used [6], in which the activity of the source being measured is compared with that of a standard source by using two identical chambers and measuring the difference in current.

The basic difficulty in methods which measure dN/dt (i.e. the activity) is that a decay curve of useful length cannot be obtained. Consequently it is not possible to be absolutely sure of the radiochemical purity and stability of the source however good the instruments may be. The risk of error can be greatly reduced by purification of the source material using well tested procedures and by using several sources prepared by different methods and having different origins.

A sounder approach to direct measurement of decay can sometimes be made by using a mass spectrometer. If for example a mixture of fission product krypton isotopes is mass analysed, at intervals of time, the ratio of $^{85}\text{Kr}/^{86}\text{Kr}$ gradually falls as the ^{85}Kr decays. In such a method no problem of radiochemical purity arises and the long term stability of the equipment and source is not involved since only a ratio is measured. It is necessary to remember that the radioactive nuclide will in cases of β emitters decay to an isobaric nuclide and the experimental condition must be such that the daughter nuclides are either eliminated from the source material or contribute nothing to the mass spectra. When measuring caesium isotopes, for example, it is possible to arrange that the barium daughters have a negligible contribution by suitably adjusting the mass spectrometer source conditions. In other cases it is possible that the source material might become contaminated with the stable isotope involved in the measurements, resulting in a spurious decrease of the ratio of decaying nuclide to stable nuclide. Since however only one element can act as contaminant this possibility can usually be tested for and guarded against. The possibility of such contamination can sometimes be checked by making measurements of other mass ratios; for example if the decay of ^{137}Cs in fission product caesium were being studied by measuring the change of the $^{137}\text{Cs}/^{133}\text{Cs}$ ratio, one could check by measuring the $^{137}\text{Cs}/^{135}\text{Cs}$ ratio and $^{135}\text{Cs}/^{133}\text{Cs}$ ratios since ^{135}Cs is infinitely long lived for the purposes of such an experiment but is a most unlikely accidental contaminant.

By such methods the half life of ^{137}Cs was measured and found to be

33 yrs [7] and that of ^{85}Kr to be 10.27 yrs [8]. Experiments have now commenced at Harwell to obtain the half life of ^{134}Cs . The ^{134}Cs was prepared by irradiating ^{133}Cs in the Materials Testing Reactor at Idaho U.S.A. The resulting material contains ^{133}Cs , ^{134}Cs and ^{135}Cs and the $^{134}\text{Cs}/^{133}\text{Cs}$ ratio is measured at intervals of three weeks. The ^{134}Cs half life has also been studied at Harwell by other methods: a value of 2.09 yrs was obtained using an automatic electroscope [9] and 2.06 yrs using an ionization chamber [10]. Values of 2.3 yrs and 1.7 yrs are given in the literature [11].

There are many cases where the direct measurement of decay is not possible, or is not sufficiently accurate, even with the best technique. In these cases we must resort to measuring both dN/dt and N and thus calculating λ . Some measurements of this type are but crude estimates, for example one might measure the activity of a nuclide produced by an (n, γ) reaction and estimate the number of atoms of the nuclide from a knowledge of the reaction cross-section and the neutron flux. In other cases a high degree of accuracy is, in principle at least, obtainable. The problem has two parts; the determination of N , the number of atoms of a given nuclide in a source; and the determination of dN/dt , the absolute disintegration rate of the source.

The methods available for determining N depend more or less directly upon weighing. When sufficient quantities of material are available the concentration of a solution can be determined by chemical analysis, or alternatively a standard solution can be prepared from a known weight of compound. The solution can then be used to provide sources for counting purposes, prepared by accurate aliquotting. Standard analytical techniques actually involve several hundred milligrams of material but it is possible to work on a milligram or even microgram scale. In extreme cases sources have been prepared on thin platinum discs and the weight of source material determined by direct weighing of the sources using an ultramicrobalance.

Weighing is an accurate operation and the chief difficulties arise from uncertainties as to the purity and stoichiometric proportions of the compounds weighed. The question of isotopic composition also arises for in many cases the nuclide being investigated will be contaminated with stable isotopes.

We can quote as an example the determination of the ^{35}Cl half life [12] where owing to the large quantity of material available the chlorine content of the solutions could be measured by ordinary gravimetric analysis but, because the ^{36}Cl was mixed with natural chlorine a mass spectrometer analysis of the chlorine was necessary. The early measurements of the ^{241}Am half life, as another example, were made on very small quantities of material. Details of the earliest measurements are not available but they depend on weighing AmO_2 in quantities which were probably in the order of micrograms, and gave values of 490 yrs [13] and 510 yrs [14]. Later measurements [15] were based on weighing platinum discs upon which AmO_2 had been deposited, the weights

of AmO_2 being in the order of 5 micrograms. These discs formed the sources used for counting. An attempt was made to set limits to the impurity content by carrying out spectrographic analysis and to confirm the stoichiometric composition of the material by X-ray diffraction measurements carried out on one of the actual sources. The value obtained was 470^{+5}_{-10} yrs. More recently this half life has been determined [16] using much larger quantities of material. In the first measurement a stock solution of ^{241}Am was prepared from which sources were prepared by pipetting from a suitably diluted solution, and the amount of americium in the solution was determined by evaporating aliquots to dryness and igniting to AmO_2 in a platinum boat. Once again the chemical purity was checked by spectrographic analysis and the stoichiometric composition by X-ray diffraction. The weights of compound used were in the order of 5 mg and the value obtained was 461.3 ± 1.7 yrs. In the second determination [17] a sample of $\text{Am}_2(\text{SO}_4)_3$ was prepared and heated to constant weight at 600°C . Preliminary work had shown that americium sulphate could be prepared as a stoichiometric compound. A weighed sample of sulphate, circa 7 mg was dissolved in dilute acid, made up to a standard solution, and counting sources were prepared as before. The value obtained was 457.6 ± 2.3 yrs.

The technique of isotope dilution using a mass spectrometer has distinct advantages over more conventional analytical methods. In this method the concentration, for example of ^{137}Cs , in a solution is determined by measuring the caesium isotopic composition of the solution before and after adding known weights of stable naturally occurring ^{133}Cs . There are three advantages in this technique. In the first place only small quantities of material are needed. Secondly it measures the concentration of the actual nuclide desired independent of chemical or isotopic contamination. Thirdly the basic weighing upon which the method depends is the weighing of the stable isotope used in making the isotope dilution. This is usually a matter of preparing a standard solution from laboratory reagents and as such does not involve microweighing or, given proper precautions, any uncertainty in the stoichiometric proportions or purity of the material weighed.

A recent determination of the ^{137}Cs half life carried out at Harwell [18] employed isotopic dilution to measure the concentration of ^{137}Cs in a solution. Analyses required only 2 microlitres of solution, containing about 10^{-8} g of caesium, although very much smaller quantities could have been used had it been necessary. Four such analyses had a standard deviation of only 0.8%.

The measurement of dN/dt will, in most cases, be a question of absolute α or β counting. Absolute α counting is best done in a low geometry counter [19]. The solid angle subtended at the source by the sensitive portion of the counter is defined by collimators and can be determined by mechanical measurement to an accuracy of 0.1%. The source must be thin, i.e. a few $\mu\text{g}/\text{cm}^2$, to eliminate self absorption of the α particles in the source material. There is no

backscattering correction since 180° scattering of α particles by the source mount is negligible and particles suffering low angle scattering from the walls of the chamber are prevented from entering the sensitive part of the counter by baffle plates. When the source contains several α emitters the absolute count of one of them can usually be obtained using an ionization chamber and pulse height analyser calibrated for α particles of various energies by use of sources standardized in low geometry counters. Indeed it is desirable to make an α pulse height analysis in any case in order to check for α emitting impurities. Inter-comparison experiments involving Harwell and Berkeley equipment showed agreement to 0.2% [20], which is essentially perfect agreement for the purposes of practical counting experiments. A discussion of precision α counting will be found elsewhere [21].

Calorimetric methods have also been applied to the determination of α half lives [22]. Provided the decay scheme and α particle energies are known a calorimetric measurement of the heat output from an α source gives a measure of dN/dt . Large sources are needed but the method is independent of the distribution of the source material, since all α particles originating inside the calorimeter are absorbed either in the source or source container. Calorimeters have also been used to observe the decay directly [23], in which case no knowledge of the α particle energies is needed. Generally calorimetric methods are tedious and no more accurate than counting methods but they do provide values which are completely independent of counting techniques.

Absolute β counting is a more difficult problem due to the shape of the typical β spectrum involving significant numbers of very low energy electrons and also due to the scattering properties of electrons. It is best met by use of a 4π type proportional counter where the source is deposited on a very thin film and supported in the centre of the (usually spherical) counter which, ideally, records all the particles leaving the source. Problems due to scattering are essentially eliminated since if an electron leaves the source it must always pass through the sensitive volume of the counter irrespective of how it might be scattered. On the other hand the absorption of the softest electrons by the mounting film and by the source material is not usually negligible and corrections must be applied.

The films are commonly made from polymers such as cellulose acetate, cellulose nitrate, methyl methacrylate, polyvinyl acetate, nylon, terylene, etc. and can be made as thin as $2\text{ }\mu\text{g/cm}^2$ although $10\text{--}50\text{ }\mu\text{g/cm}^2$ is a more usual figure. These films must be rendered electrically conducting which has been done by coating them with gold or aluminium in a vacuum sublimation apparatus. Some workers suggest that a thickness of gold of $2\text{ }\mu\text{g/cm}^2$ on one side is sufficient whilst others suggest that at least $10\text{ }\mu\text{g/cm}^2$ on both sides is necessary. The most recent work indicates that carbon will be superior to gold for rendering films conducting. Aluminium sheet can be obtained com-

mercially of thickness $250\text{ }\mu\text{g}/\text{cm}^2$ which is very convenient since it does not require treatment to make it conducting. The correction factors for β emitters of various energies can be measured by making counts on films of different thickness and extrapolating to zero thickness. The corrections for a $50\text{ }\mu\text{g}/\text{cm}^2$ film are about 9% for ^{63}Ni (maximum β energy 0.07 MeV), 2% for ^{35}S (maximum β energy 0.17 MeV) and 0.5% for ^{204}Tl (maximum β energy 0.76 MeV). The problem thus becomes rapidly less serious as the β energy increases.

The correction for self absorption is difficult to assess. Sources are normally prepared by evaporating to dryness small accurately measured volumes of solution. One might hope that by using material of very high specific activity and hence sources of very low weight the self absorption would be rendered negligible. This is not necessarily the case however because as one reduces the weight of the source there comes a point when the crystals formed by evaporation do not become smaller with decreasing source weight i.e. the number of crystals is less but not their size. In any case there is often a limit to the dilution at which one can work due to the risk of absorption of materials onto the wall of flasks, pipettes, etc. In the counting carried out for the ^{137}Cs half life determination at Harwell [18] the sources weighing from 0.05 to $1.0\text{ }\mu\text{g}$ had identical observed specific activities although heavier sources showed losses (compared to the light sources) of around 0.5% for a $2.5\text{ }\mu\text{g}$ source and 2.0% for a $5\text{ }\mu\text{g}$ source. Whilst this indicates that self absorption could not have been large it does not prove that it was negligible. In particular cases sources can be prepared by sublimation or electrodeposition in which case they are much more uniform in thickness and provided they are of small weight (few μg) self absorption should be negligible. In a few cases an absolute β count can be obtained by β - γ coincidence methods which are not affected by self absorption losses, and by intercomparison the losses for crystalline sources and film absorption can be estimated. In the case of ^{60}Co (maximum β energy 0.32 MeV) an aluminium foil of $250\text{ }\mu\text{g}/\text{cm}^2$ caused a loss of 5% and the self absorption of crystalline sources was $4\div 5\%$ for sources of a few μg weight. In the case of ^{24}Na (maximum energy 1.4 MeV) the combined losses for a source of comparatively large crystals on similar foil was around 2%. Once again the difficulties decrease rapidly with increasing β energy. The use of insulin as a spreading agent in preparing sources from solution has much to recommend it. In some cases, at least, the problem of crystal size seems to be largely eliminated by using insulin and it is possible to obtain a self absorption curve (plot of specific activity versus weight of source) extending down to at least $0.5\text{ }\mu\text{g}$ sources which shows a small but steady increase in observed specific activity over the very lowest range of weights. In general a good source of a β emitter of maximum energy about 0.5 MeV is not likely to have more than 1% self absorption. The greater difficulty in absolute β counting as compared to α is reflected in the results of inter-comparison exper-

iments between different laboratories which often reveal discrepancies of several percent. The techniques for making thin films are described in ref. [25] whilst ref. [26] gives a series of papers in which 4π counting is described very completely.

If the half life is extremely long it will not be possible to obtain a « weightless » source with a useful counting rate. It may then be necessary to use a thick source, say 10 mg/cm^2 in an internal source 2π type counter or some form of windowed counter and to estimate the absorption and scattering corrections from experiments on sources of a similar nature prepared from other β emitters of similar energy and of known activity. In this case the β count might be obtained with an accuracy of perhaps $\pm 20\%$ [30-32].

When making absolute β counts it is necessary to study the decay scheme of the β emitter. Many β emitters emit γ -rays which are not coincident with the β -particle (i.e. from short lived isomeric states of the daughter nuclide) and these γ -rays may be counted by the 4π counter partly because of the electrons they produce in the counter walls and gas and, more important, because they can be internally converted giving conversion electrons. The efficiency for counting the unconverted γ -rays is small, but the conversion electrons are of course counted with virtually 100% efficiency. For example in 4π counting of ^{137}Cs the γ -rays from $^{137}\text{Ba}^m$ (2.6 min) contribute 0.098 counts per true β count due to being internally converted but only about 0.002 counts per true β count due to direct counting of the unconverted γ -rays. The nuclide studied may also decay to a β or α active daughter. β active daughters do not present any serious problem provided their presence is recognized and the proportion of decays leading to them (usually 100%) is known. The presence of α emitting substances is very detrimental to 4π counting for the pulses they produce under β counting conditions are so large and of such long duration that they obscure a proportion of the comparatively very small β pulses. Once again it may be necessary to resort to windowed counters and to use absorbers.

We cannot subject β particles to pulse height analysis as we do α particles which means that it is very difficult to prove that a long lived β emitter is radiochemically pure. Evidence can be collected however, from absorption curves, β -ray spectroscopy and γ -ray spectroscopy. Many impurities can be detected by counting carrier substances which have been added to and then isolated from the material under study. A most important test is to measure the specific activity of the material before and after carrying out radiochemical purification procedures. If possible determinations should be repeated using materials of different origin and treatment.

It is probably true to say that few half lives are known with certainty to better than $\pm 1\%$. In the case of moderate half lives where decay can be followed over several half-lives the statistical accuracy of the results is often

better than this limit; indeed, even with half lives in the order of years the instrumental work may be so good as to indicate a value better than $\pm 1\%$. Often however there remains some doubt, especially as to the radiochemical purity of the material. Contamination by radioactive substances having a half life rather close to that of the nuclide being studied is very hard to detect by a study of decay curves. Such doubts are most convincingly removed when various workers, preferably using different techniques, produce values in good agreement and when positive proof of radiochemical purity is obtainable. The half life of ^{198}Au for instance is probably known to better than $\pm 0.1\%$ [27].

With very long half lives the possibility of error is greater because of difficulties, which we have described, regarding radiochemical purity, stoichiometric proportions, absolute β counting etc. The values we have quoted for ^{241}Am show fairly convincingly that this half life at least is known to $\pm 1\%$ or better. On the other hand the ^{137}Cs half life has been measured recently at McMaster University to be 26.6 yrs [28] whereas the Harwell result, obtained using the same method, was 30.0 yrs [18] and the previously accepted value was 33 yrs [7]. Similarly the most recent value for the ^{90}Sr half life is 27.7 yrs [29] whereas previous values (quoted in reference [29]) include 30 yrs, 25 yrs and 19.9 yrs. Evidently much work remains to be done in this field, particularly by groups of workers who are in a position to undertake long term measurements.

REFERENCES

- [1] G. B. COOK and J. F. DUNCAN: *Modern Radiochemical Practice* (Oxford, 1952).
- [2] R. M. BARTHOLOMEW, F. BROWN, W. D. HOWELL, W. R. J. SHOREY and L. YAFFE: *Canad. Journ. of Phys.*, **31**, 714 (1953).
- [3] F. J. STUBBS and G. N. WALTON: *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, **7**, 163 (1955).
- [4] G. R. CHOPPIN, S. G. THOMPSON, A. GHIORSO and B. G. HARVEY: *Phys. Rev.*, **94**, 1080 (1954).
- [5] B. ROSE and J. MILSTED: *Journ. of Nucl. Energy*, **2**, 264 (1956).
- [6] J. TOBAILEM: *Compt. Rend.*, **233**, 1360 (1951); *Journ. Phys. et Rad.*, **16**, 48 (1955).
- [7] D. R. WILES, B. SMITH, R. HORSLEY and H. G. THODE: *Canad. Journ. of Phys.*, **31**, 419 (1953).
- [8] R. K. WANLESS and H. G. THODE: *Canad. Journ. of Phys.*, **31**, 517 (1953).
- [9] C. G. CAMPBELL: private communication.
- [10] E. E. LOCKETT: private communication.
- [11] I. M. HOLLANDER, I. PERLMAN and G. T. SEABORG: *Rev. Mod. Phys.*, **25**, 469 (1953).
- [12] R. M. BARTHOLOMEW, A. W. BOYD, F. BROWN, R. C. HAWKINGS, M. LOUNSBURY and W. F. MERRITT: *Canad. Journ. of Phys.*, **33**, 43 (1955).

- [13] B. B. CUNNINGHAM and R. C. THOMPSON: *An Inst. Bibl. of Atom. Energy*, vol. 2, n. 6955.
- [14] B. B. CUNNINGHAM: NNES, IV Vol. 14B, paper 19.2 (New York, 1949).
- [15] B. G. HARVEY: *Phys. Rev.*, **85**, 482 (1952).
- [16] G. R. HALL and B. I. MARKIN: *Journ. of Inorg. and Nucl. Chem.*, **2**, 202 (1956).
- [17] G. R. HALL and B. I. MARKIN: to be published.
- [18] F. BROWN, G. R. HALL and D. N. WALTER: *Journ. of Inorg. and Nucl. Chem.*, **1**, 241 (1955).
- [19] R. HURST, G. R. HALL and K. M. GLOVER: *A.E.R.E. C.R.* 647.
- [20] K. M. GLOVER and G. R. HALL: *Nature*, **173**, 991 (1954).
- [21] R. HURST and G. R. HALL: *The Analyst*, **77**, 790 (1952).
- [22] E. F. WESTRUM, J. C. HINDMAN and G. W. GREENLEE: NNES IV, Vol. 14B, paper 22-80 (New York, 1949).
- [23] O. S. HUTCHISON and L. WHITE: *A.E.R.E. C.R.* 1365.
- [24] R. F. SMITH: *A.E.R.E. I/R* 1527.
- [25] B. D. PATE and L. YAFFE: *Canad. Journ. of Chem.*, **33**, 15 (1955).
- [26] B. D. PATE and L. YAFFE: *Canad. Journ. of Chem.*, **33**, 610, 929, 1656 (1955); **34**, 265 (1956).
- [27] R. E. BELL and L. YAFFE: *Canad. Journ. of Phys.*, **32**, 416 (1954).
- [28] D. M. WILES and R. H. TOMLINSON: *Phys. Rev.*, **99**, 188 (1955).
- [29] D. M. WILES and R. H. TOMLINSON: *Canad. Journ. of Phys.*, **33**, 133 (1955).
- [30] G. N. WALTON, S. G. THOMPSON and R. N. CROALL: *A.E.R.E. C.R.* 1136.
- [31] J. S. BOWLES and G. N. WALTON: *A.E.R.E. C.R.* 1463.
- [32] J. G. CUNNINGHAME, M. L. SIZELAND and H. H. WILLIS: *A.E.R.E. C.R.* 1646.

The Lattice Constants of Small Crystals.

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1. - Introduction.

During the last two decades, a number of attempts have been made to detect a difference between the structure of very small crystals and those of normal size. It is, of course, to be expected that such differences will occur. Atoms on the surface of a crystal have a different environment from those in the interior and therefore when in equilibrium would be expected to have a different spacing. Thus, LENNARD-JONES and DENT [7] calculated that a single 100 plane of an alkali halide should have an interatomic spacing some 5% smaller than a similar plane in the interior of the crystal. To keep the surface atoms in line with those in the interior, there must be reactions between the surface and interior which are equivalent to a surface tension $\sim +2000$ dyn/cm. More recently, NICOLSON [8] has calculated the unbalanced forces on the atoms in a 100 surface of an alkali halide and has arrived at a similar order of magnitude for the surface tension. On the other hand, SHUTTLEWORTH [14], by a different method, has obtained values ~ -300 dyn/cm for the surface tension in 100 alkali halide planes.

A positive surface tension implies that the interior of the crystal will be compressed. Small crystals would then have a smaller lattice constant than large ones. Conversely, a negative surface tension causes small crystals to have a relatively large lattice constant. The pressure within a spherical crystal of diameter D subjected to a surface tension γ is $4\gamma/D$. If the bulk modulus of the material is K , the fractional change in volume is $-4\gamma/KD$ and the fractional change δ in lattice constant is therefore

$$(1) \quad \delta = -4\gamma/3KD.$$

The first experimental study of small crystals was made by FINCH and FORDHAM [2] who used electron diffraction to compare the lattice constants

of vacuum evaporated alkali halide specimens with that of gold leaf, which was used as a standard. They found some indication that the lattice constants of small crystals were less than those of large ones, corresponding to a positive surface tension.

BOSWELL [1] has made the most extensive measurements. He compared the lattice constants of alkali halides with standards of graphite and thallous chloride. The size of the crystals was deduced from the breadth of the diffraction rings. Fig. 1, which is plotted from his results, would suggest that the change in lattice constant is inversely proportional to the size of the crystal in accordance with equation (1). The slope of the line in Fig. 1 would correspond to a surface tension of -2400 dyn/cm. On the other hand, HALLIDAY, RYMER and WRIGHT [6], using an entirely different electron-diffraction technique, obtained a value of -750 dyn/cm for the surface tension of the same material.

It is apparent that neither theoretical nor experimental physicists are in agreement among themselves as to the sign of the effects observed in small crystals. It is the purpose of this paper to explain the reason for this disagreement, and to point to its solution.

2. - Technique of measurement of lattice constants by electron diffraction.

Most studies of small crystals have been made by transmission electron diffraction. X-ray diffraction is not very suitable for the study of the smallest crystals because the resulting diffuseness of the lines introduces large errors into the measurements. We shall therefore confine our attention to electron diffraction measurements. An electron beam passes through a thin specimen and strikes a photographic plate at a distance L . The radius of a diffraction ring R is related to the electron wave-length λ and the interplanar spacing d by the equation

$$(2) \quad \lambda L = Rd(1 - \frac{3}{8}R^2/L^2).$$

To determine d from this equation is necessary to measure both R and λL . RYMER and WRIGHT [13] and HALLIDAY, RYMER and WRIGHT [6] have mea-

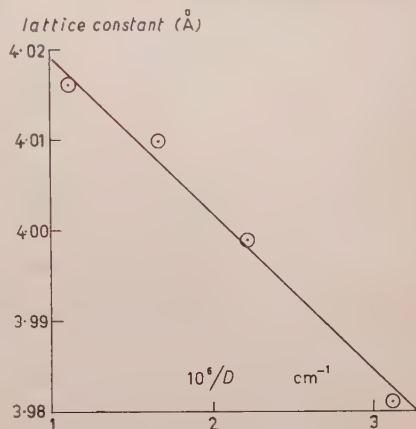


Fig. 1. - Boswell's measurements of the apparent change of lattice constant of lithium fluoride with crystal size, D .

sured L directly and derived λ from an accurate potentiometric measurement of the voltage applied to the electron gun. The last is a difficult measurement and therefore other observers have used a comparison method in which λL is determined by a subsidiary experiment using a specimen with known interplanar spacing. For this purpose, a material having large crystals ($\sim 1000 \text{ \AA}$) and giving sharp diffraction rings is used. It is assumed that surface tension and other effects are negligible for such large crystals and that the lattice constant is that given by the best X-ray measurements.

The following [11, 13] are the principal sources of error in the determination of the diffraction ring radius:

1) The intensity is greater on the inner side of a broad diffraction ring than the outer owing to the shorter perimeter into which it is concentrated. This results in an inward displacement of the maximum.

2) A diffuse background whose intensity diminishes with distance from the centre of the pattern produces an inward displacement of the diffraction ring maximum.

3) Stray non-uniform magnetic or electric fields in the space between specimen and plate distort the rings into ellipses but do not affect the average radii of the rings. Along any diameter of the pattern, the effect of such fields is to produce a change of scale of the pattern.

4) If the undiffracted beam strikes the photographic plate, it charges it up and the resulting electrostatic field increases the radii of the diffraction rings by amounts inversely proportional to their original values.

5) An electric charge on the specimen changes the scale of the diffraction pattern; an asymmetrical patch of charge may produce elliptical diffraction rings.

Corrections can be made for many of these errors [11] but this has been neglected by most observers.

The size of the crystals is determined by measuring the width of the diffraction rings, making any necessary correction for the finite width of the focussed electron beam and any other instrumental effects. It is assumed that the only factor producing broadening of the diffraction rings is the finite size of the crystals. Under these conditions, the integral width w of a ring (i.e. the area under the intensity contour divided by the peak intensity) is related to the volume average thickness T of the crystal measured perpendicular to the reflecting planes by the equation [15]

$$(3) \quad T = (\lambda L)/w.$$

If the specimen consists of crystals of different sizes and shapes, T is the volume average thickness of all the crystals. By measuring the widths of diffraction rings of different indices, it should thus be possible to determine both the average size and shape of the crystals. If this procedure is to be valid, there must be no source of ring broadening other than the finite size of the crystals.

The possible sources of ring broadening, besides finite crystal size, are variation of lattice constant from one crystal to another due to non-homogeneous stresses in the specimen, refraction at the crystal surfaces and dynamical interference effects. It should, in principle, be possible to distinguish between particle-size and strain broadening by comparing the widths of different order reflexions from the same set of planes. Particle-size broadening will be the same for all orders but strain broadening will be greater for the higher orders. The difficulty in practice is that there is usually insufficient contrast between second and higher order reflexions and the general diffuse background for the width of the former to be reliably determined. The diffuse background is mainly due to inelastically scattered electrons, and there is evidence that the proportion of these diminishes as the energy of the primary electrons is increased. The recent development in several laboratories of electron-diffraction cameras operating at several hundred kV, instead of the usual 50-100 kV, may make it possible in future to obtain reliable measurements of the widths of several orders of reflexion. The use of higher voltages would have the additional advantage that broadening due to refraction and dynamical interference effects would be reduced to negligible proportions.

Another method of distinguishing between particle-size and strain broadening has been suggested by WARREN and AVERBACH [16]. These authors express the (symmetrical) intensity contour of a ring in the form of a Fourier series

$$I(x) = \sum a_n \cos nx,$$

where the scale of distance x on the photographic plate is so chosen that the distance between successive orders of the same reflexion is 2π . They show that for particle-size broadening

$$(da_n/dn)_{n=0} < 0.$$

For all other types of broadening, it may be shown that

$$(da_n/dn)_{n=0} = 0.$$

Unfortunately, the value of $(da_n/dn)_{n=0}$ is determined by the shape of the « wings » of the line, which is difficult to determine with any accuracy in the

presence of a diffuse background. It is therefore hardly worth while carrying out a Fourier analysis of the line contour. Unpublished work of RYMER and FAYERS indicates that there is, however, a perceptible difference between the contours due to particle-size and other types of broadening. The latter are always closely Gaussian in form over a wide range of intensity; the former have departed perceptibly from Gaussian form at intensities of about 10% of the maximum. The difference is shown in Figs. 2 and 3 which show the contours of diffraction rings broadened by random stresses and by particle size respectively. A high resolution camera was used having a focussed spot size less than $10\text{ }\mu\text{m}$. Instrumental broadening is therefore negligible. Fig. 2

represents a contour which is accurately Gaussian over more than a hundred-fold range of intensity; Fig. 3 represents a contour which has departed appreciably from Gaussian form at intensities exceeding 10% of the maximum.

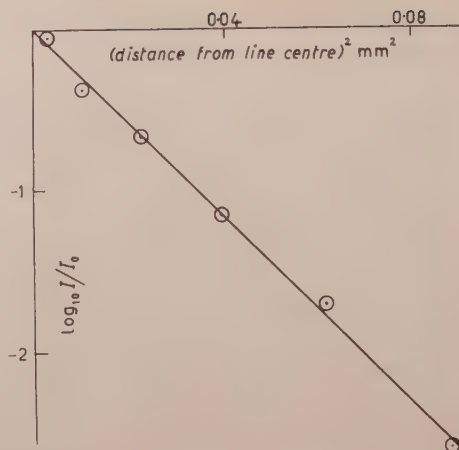


Fig. 2. — Intensity contour of 200 reflexion from a specimen of vacuum evaporated copper. The contour is Gaussian over a hundredfold range of intensity, indicating that the breadth is mainly due to strains.

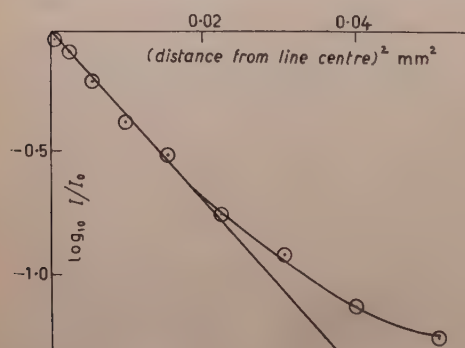


Fig. 3. — Intensity contour of 220 reflexion from a specimen of vacuum evaporated lithium fluoride. The contour departs from Gaussian form at intensities exceeding 10% of the maximum, indicating that the breadth is mainly due to particle size.

3. — Results of electron-diffraction measurements of lattice constants.

For the sake of brevity, we shall consider only a few typical electron-diffraction studies. Results by other workers are either in general agreement with those mentioned here, or else are of low accuracy owing to neglect of the systematic sources of error mentioned in Sect. 2.

HALLIDAY, RYMER and WRIGHT [6] made a study of lithium fluoride films. A special measuring technique [11] was used which corrected errors (1) and (2) due to line curvature and diffuse background. Stray field errors (3) were eliminated by averaging the results of measurements along at least 9 different diameters. The undiffracted beam was intercepted to prevent the photographic plate charging up (4). An electron spray was used to prevent the specimen charging up; its effectiveness was demonstrated in the work of RYMER and WRIGHT [13] who found that specimens of sodium and potassium chlorides and caesium iodide examined in the same camera had lattice constants within 0.01% of the X-ray values. For many of the observations the «camera constant» λL of equation (2) was determined by direct measurement of L and a potentiometric measurement of the voltage applied to the electron gun. It was found that the ratios of the interplanar spacings d_{hkl} of different planes hkl were not those of undistorted cubic crystals but were consistent with elastic deformation of the crystals under the action of three mutually perpendicular tensions. Two of these, having a certain magnitude p , lay in the plane of the specimen and the third, of magnitude $2.5p$, was perpendicular to the plane of the specimen. The authors pointed out that if the material were in the form of long cylinders of radius r with axes perpendicular to the specimen plane, then a surface tension γ would produce a tension along the cylinder of magnitude $-2\gamma/r$ and two tensions $-\gamma/r$ in perpendicular directions. They suggested that the 2:1 ratio of longitudinal to transverse tensions might be increased to the observed value of 2.5:1 if the cross-sections of the cylinders were not smooth but were wrinkled. It has been pointed out in Sect. 2 that the contour of the diffraction rings (Fig. 3) makes it probable that their width is due solely to the small size of the crystals. If these are identified with the cylinders, then comparison of the ring widths with the tensions p leads to a determination of the surface tension γ . In this way, the authors found the surface tension of lithium fluoride to be -750 dyn/cm. No doubt, objections can be raised to the conception of a division of the material of the specimen into cylinders subject to surface tension. However, the measurements (which were made by a well-tried method shown to be capable of an accuracy of 0.01%) show clearly that the specimen behaves as if it were subject to a tension and therefore has a lattice constant higher than normal. This increase of lattice constant is greater for those specimens giving broader diffraction rings and therefore consisting of smaller crystals. It is impossible to reconcile these two facts with a positive surface tension. Thus, although the *magnitude* of the surface tension may be open to question, its *sign* appears to be clearly determined. The size of the crystallites ranged from about 50-120 Å. No other alkali halides were examined in this investigation, but RYMER and WRIGHT [13] found that sodium and potassium chloride and caesium iodide had normal lattice constants. The crystal size of these specimens was not stated in the paper referred to; it was, in fact, in no case less than 100 Å.

The observations of BOSWELL [1] make an interesting contrast to those discussed above. This author examined, among other materials, sodium and potassium chloride, sodium bromide and lithium fluoride. A comparison method was used, patterns being obtained in succession from the material under test and from a standard of thallium chloride. No allowance was made for any of the errors discussed in Sect. 2 and therefore the results are of a lower order of accuracy than those described above. On the other hand, the range of crystal size was much greater ($18 \div 150 \text{ \AA}$) and apparent changes of lattice constant up to 1% were observed. This is larger than any probable error of measurement and corresponds to a *decrease* of lattice constant with diminution of crystal size, in direct contradiction with the results of HALLIDAY, RYMER and WRIGHT. Of the various sources of error previously discussed, the only ones which are likely to vary in a consistent manner with crystal size (or ring width) are those due to line curvature (1) and diffuse background (2), both of which will increase with the width of the rings. Such errors, however, would correspond to an apparent *increase* of lattice constant for small crystals (since they both result in an inward displacement of the peaks of the diffraction rings). BOSWELL's results cannot, therefore, be seriously affected by experimental errors of this kind. It is probable that their explanation is to be found in the extreme smallness of the crystals in his specimens. GERMER and WHITE [4] have pointed out that in the usual theory of diffraction by small crystals, summation of the waves scattered by the separate atoms is replaced by an integration over a crystal bounded by a mathematically smooth surface. This is unimportant for larger crystals having only a negligible proportion of atoms near the surface, but is inappropriate for very small crystals: a smooth surface is then a very poor approximation to the real assembly of separate atoms. It is better to regard such small crystals as single large molecules and to treat the problem in terms of the Debye theory of diffraction by gas molecules. GERMER and WHITE calculated the diffraction patterns produced by face-centred cubic crystals of different sizes and showed that for crystals containing less than about 50 unit cells the 200 reflexion is weaker than for large crystals, in agreement with their measurements of diffraction patterns of copper oxide. The theoretical diffraction patterns published by GERMER and WHITE suggest that the radii of the diffraction rings are slightly increased when the crystals are small. This has been confirmed by using their theory to calculate the diffraction pattern from an assembly of cubic crystals each having a side of length 2 unit cells. It has been found that the radius of the 111 diffraction ring is 2.8% greater than that of large crystals, corresponding to an apparent decrease of lattice constant for small crystals of similar magnitude to that found by BOSWELL. This is illustrated in Fig. 4, which shows BOSWELL's results in synoptic form. It will be seen that, with the exception of the potassium chloride measurements, all the points lie near to the straight line representing

the apparent change of lattice constant according to the theory of diffraction by gas molecules. The agreement of theory and experiment would be improved if the points were displaced to the left. This would occur if one increased BOSWELL's estimate of the instrumental contribution to the breadth of the diffraction rings. This seems justified since BOSWELL claims a focussed spot size as low as $10\text{ }\mu\text{m}$, but gives no indication that it was actually measured. If the apparent change of lattice constant were a real phenomenon due, for example, to surface tension forces, its magnitude would depend on the interatomic forces and would therefore be different for different materials. The fact that the magnitude of the effect is the same for all the substances examined points to a more fundamental origin and tends to support the theory of diffraction by gas molecules.

It is concluded that specimens with a crystal size less than about $50\text{ }\text{\AA}$ are unsuitable for a study of the dependence of lattice constant on crystal size owing to the failure of crystal diffraction theory when applied to such small particles. For crystals larger than this, the effects expected are too small to be reliably detected except by measurements of the highest precision. It is thought that the only sure evidence for a variation of lattice constant is provided by the measurements on lithium fluoride [6] described above, which indicate an increased lattice constant for small crystals and therefore a negative value for the surface tension.

4. - Theories of surface tension of solids.

In Sect. 1, reference was made to the calculations of LENNARD-JONES and DENT [7] and of NICOLSON [8]. Both these calculations lead to an estimate of the resultant forces on the atoms in a 100 surface of an alkali halide *when these occupy the same relative positions as the atoms in the interior*. This is, however, not a true measure of the surface tension. Under the action of the resultant force, the surface atoms will move to new equilibrium positions and

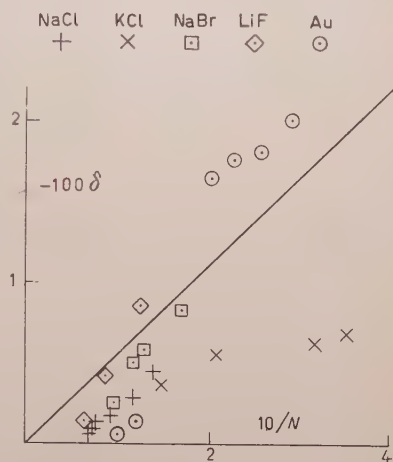


Fig. 4. - Boswell's measurements of the apparent change in lattice constant with crystal size. The fractional change in lattice constant δ is plotted against the reciprocal of N , the linear dimension of the crystals divided by the side of the unit cell. The straight line joins the origin to the point $N=2$; $\delta = -2.8\%$. This value is obtained by treating the problem as one of diffraction by a gas.

their reaction on the interior of the solid, which constitutes the surface tension stress, will be changed. Moreover, if lattice vacancies occur and can diffuse through the solid, the concentration of vacancies at the surface may differ from that in the interior, resulting in a further change in the reaction of the surface on the interior. Attention was drawn to the first of these considerations by SHUTTLEWORTH [14], who pointed out that if F is the surface free energy of the solid, i.e. the mechanical work required per unit increase of surface area, γ the surface tension and A the surface area,

$$\gamma dA = d(FA)$$

and therefore

$$(4) \quad \gamma = F + A \frac{dF}{dA}.$$

Now F is essentially positive, for it is related to the energy of cohesion of the solid. This may be seen when it is remembered that the division of a solid into two pieces followed by their separation can be regarded as equivalent to a change in the surface area. The quantity dF/dA is essentially negative, for the surface free energy will diminish if the inter-atomic spacing of the surface atoms is increased. Thus the sign of the surface tension γ will depend on the relative magnitudes of F and $A dF/dA$. According to the detailed calculations of SHUTTLEWORTH, these quantities are of the same order of magnitude and their difference is probably negative for most alkali halides.

A different theory of surface tension has been advanced by GURNEY [5] who has pointed out that in a solid in thermal equilibrium at a temperature above the absolute zero there will be vacant lattice sites. Further, the thermodynamic potential of a surface atom is greater than that of one in the interior. Surface atoms will therefore be lost to the interior by diffusion of vacancies to the surface. The concentration of surface atoms will be determined by thermodynamic equilibrium between surface and interior and will therefore not change if the surface area is increased. Since the surface free energy is determined by the concentration of surface atoms, the third term in equation (4) will be zero and we shall have

$$(5) \quad \gamma = F.$$

The surface tension is then essentially positive. This is also evident when it is remembered that surface atoms are assumed to be lost to the interior and therefore the mean inter-atomic distance is greater in the surface layer, which will therefore be in a state of tension.

The assumptions made in these three theories of solid surface tension, and

the order of magnitude of the surface tension of the alkali halides which they predict, may be summarized as follows:

Perfect, undistorted lattice extending to the surface [7, 8]	+ 5 000 dyn/cm;
Surface atoms free to take up new equilibrium positions, but no extra surface vacancies [14] —	500 dyn/cm;
Surface atoms in thermodynamic equilibrium with the interior [5]	+ 1 500 dyn/cm.

The experimental results discussed in Sect. 3 indicate that the second of these theories is in closest accord with the facts. It would be unrealistic to assume that the crystals of vacuum evaporated films are free of vacancies. It is more likely that each layer of atoms is deposited with a concentration of vacancies appropriate to a surface layer, and that there is no outward diffusion of excess vacancies when further layers are deposited. The whole crystal therefore has a concentration of vacancies appropriate to surface layers, and greater than the equilibrium concentration for a large crystal.

5. — Distortion of crystals by lattice defects.

In the previous sections, we have interpreted observations on small crystals in terms of distortions due to surface tension forces. It should be pointed out, however, that crystals prepared by vacuum evaporation contain defects which can distort the diffraction pattern. RYMER, FAYERS and HEWITT [12] have shown that the radii of the diffraction rings produced by vacuum evaporated silver specimens are in exact agreement with the theory [9] of diffraction by a lattice containing stacking faults. RYMER [10] has studied the diffraction patterns of vacuum evaporated gold and aluminium and found that they are in agreement with a theory of diffraction by a lattice containing a sessile [3] dislocation. It is clearly necessary to be very cautious in attributing distortions of diffraction patterns to surface tension forces. It is necessary to test that the displacement of a particular diffraction ring changes with crystal size. Surface tension forces should produce displacements inversely proportional to the crystal size and therefore proportional to the breadth of the ring (assuming that finite crystal size is the sole cause of the ring breadth). It should also be verified, by a study of the intensity profile or otherwise, that the breadth of the diffraction rings is due to the finite size of the crystals. Finally, the relative displacements of the diffraction rings should be studied to see whether they are consistent with the assumption of a system of stresses which can

reasonably be ascribed to surface tension. The only measurements known to satisfy all these tests are those on lithium fluoride discussed in Sect. 3.

The calculation [10] of the effect of a sessile dislocation on the diffraction pattern is of interest. The following expression is given for the change $\delta\theta$ in the Bragg reflexion angle θ due to lattice distortions:

$$(6) \quad \frac{\delta\theta}{\theta} = - \frac{\sum (p_n - p_m)(P_n - P_m)}{\sum (P_n - P_m)^2},$$

P_n is the co-ordinate of the n -th atom in the undistorted crystal measured perpendicular to the reflecting planes; p_n is the displacement of this atom in the same direction due to the distortion. The displacements of the atoms due to the sessile dislocation are obtained by assuming the crystal to be an elastic continuum subjected to a «double force» at the position of the dislocation; the determination of the displacements is then a standard problem in the theory of elasticity.

The effect of lattice vacancies or interstitial atoms on measurements of lattice constant—a question relevant to X-ray-pyknetric studies—can be estimated in a similar manner. Consider a spherical crystal of radius R_0 containing at its centre a cavity of radius r_0 . Let the cavity shrink to zero so that strains are set up in the crystal. This type of distortion constitutes a «centre of dilatation». The radial displacement δr of an atom at distance r from the centre can be calculated from standard elasticity theory and is found to be

$$(7) \quad \delta r = -r_0^3 \left[\frac{1}{r^2} + \frac{2r}{R_0^3} \frac{1-2\nu}{1+\nu} \right],$$

where ν is Poisson's ratio.

The change in the Bragg angle given by (6) when atomic displacements of the form (7) are assumed can be shown to correspond to an apparent *decrease* of lattice constant by a fraction

$$\frac{3(3-\nu)}{1+\nu} \left(\frac{r_0}{R_0} \right)^3,$$

and therefore to a decrease of the volume of the unit cell by a fraction

$$\frac{9(3-\nu)}{1+\nu} \left(\frac{r_0}{R_0} \right)^3.$$

Now $(r_0/R_0)^3$ is the ratio of the original volume of the cavity to that of the whole crystal and is of the order of the ratio of the number of missing atoms to the total number. Taking $\nu = \frac{1}{4}$ as an average value for Poisson's ratio

shows that the reduction in the volume of the unit cell is approximately 20 times the fraction of atoms missing. It is to be expected that in a larger crystal containing widely separated vacancies, the resultant change in lattice constant will be of similar magnitude, i.e. an order of magnitude greater than the proportion of vacancies. Interstitial atoms will be expected to produce an increase of lattice constant of similar magnitude. This result assumes that the defects are uniformly distributed throughout the crystal so that an approximately equal volume is associated with each, and these volumes do not overlap. The same method of calculation shows that for a random distribution of defects, the fractional change in the volume of the unit cell is equal to the proportion of defects.

It therefore appears that, in the X-ray-pyknometric method of determining Avogadro's constant, vacancies and interstitial atoms will affect the result through lattice distortion to an extent which depends critically on their distribution, and which is usually appreciably greater than the proportion of defects.

REFERENCES

- [1] F. W. C. BOSWELL: *Proc. Phys. Soc.*, A **64**, 465 (1951).
- [2] G. I. FINCH and S. FORDHAM: *Proc. Phys. Soc.*, **48**, 85 (1936).
- [3] F. C. FRANK: *Proc. Phys. Soc.*, A **62**, 202 (1949).
- [4] L. H. GERMER and A. H. WHITE: *Phys. Rev.*, **60**, 447 (1941).
- [5] C. GURNEY: *Proc. Phys. Soc.*, A **62**, 639 (1949).
- [6] J. S. HALLIDAY, T. B. RYMER and K. H. R. WRIGHT: *Proc. Roy. Soc.*, A **225**, 548 (1954).
- [7] J. E. LENNARD-JONES and B. M. DENT: *Proc. Roy. Soc.*, A **121**, 247 (1928).
- [8] M. M. NICOLSON: *Proc. Roy. Soc.*, A **223**, 490 (1955).
- [9] M. S. PATERSON: *Journ. Appl. Phys.*, **23**, 805 (1952).
- [10] T. B. RYMER: *Proc. Roy. Soc.*, A **235**, 274 (1956).
- [11] T. B. RYMER and C. C. BUTLER: *Phil. Mag.*, **36**, 515, 821 (1945).
- [12] T. B. RYMER, F. J. FAYERS and S. J. HEWITT: *Proc. Phys. Soc.*, B **69**, 1059 (1956).
- [13] T. B. RYMER and K. H. R. WRIGHT: *Proc. Roy. Soc.*, A **215**, 550 (1952).
- [14] R. SHUTTLEWORTH: *Proc. Phys. Soc.*, A **63**, 444 (1950).
- [15] A. R. STOKES and A. J. C. WILSON: *Proc. Camb. Phil. Soc.*, **38**, 313 (1942).
- [16] B. E. WARREN and B. L. AVERBACH: *Journ. Appl. Phys.*, **21**, 595 (1950).

Absolute Precision Measurements of Nuclear Energy Levels and their Breadths in Terms of Fundamental Atomic Constants.

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1. - Introduction.

Among the various characteristic quantities by which a nuclear energy level is described the energy and the breadth of the level are important. Particularly the energies of certain narrow levels have to be known accurately since they serve as standards for the determination of reaction Q values, thereby affecting for instance the mass values of nuclei. The work reported here has been done at the University of Zürich by F. BUMILLER, J. W. MÜLLER, H. E. WEAVER and the author.

Heretofore [1-5] these energies with one exception had been determined by electrostatic deflection and in the case of the $\text{Li}(\text{pn})$ threshold by time of flight method [6]. In the present measurement the energy of the incident protons is determined by deflection in a homogeneous magnetic field, whose value and configuration can be measured with a very high degree of accuracy with nuclear magnetic resonance. Moreover this method is free from difficulties arising from end effects at the entrance and exit slits and effects due to charging up of the deflecting plates.

2. - Apparatus.

Fig. 1 shows the general arrangement of the apparatus which is described in detail elsewhere [7]. The deflecting magnet is a circular sector of about 200° with a mean radius of 50 cm, a gap of 12 mm and a pole width of 70 mm. The pole pieces are kept together by 27 C yokes each carrying a separate additional winding for current shimming. In this manner the field along the orbit

of the protons does not vary by more than 1 part in 10 000 about its average. This variation which can be easily measured has been corrected for. Entrance and exit slits are mounted on a rigid temperature controlled bar and are placed within the homogeneous part of the field through two flanged openings of the spectrometer vacuum chamber. At 90° deflection an aperture slit limits the

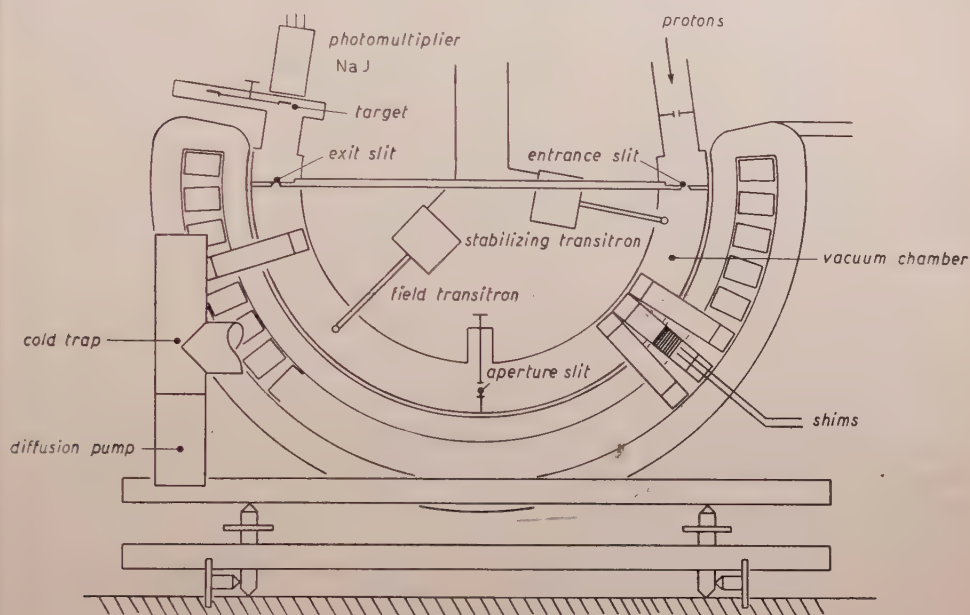


Fig. 1.

angular spread. The magnet current is electronically stabilized and the value of the field is kept constant to within 1 part in 30 000 by a nuclear resonance signal derived from a transitron [8] probe arranged in a small recess of the vacuum chamber. After passing through the exit slit the protons impinge on the target consisting of material evaporated in vacuo on silver backing. To avoid contamination of the target by condensible material, the target is heated to about 200 °C by a radiator placed in its back. A NaI scintillation counter and a 5819 photomultiplier are arranged close to the target for γ counting. The energy of the protons accelerated by the University of Zürich electrostatic generator is kept constant to about 1 kV at 1 MV. Total bombarding charges are measured by a current integrator.

For the determination of the shape of the very narrow $^{27}\text{Al}(\text{p}\gamma)$ resonance the energy of the protons incident on the target was varied by changing the target potential rather than altering the deflecting field. This was accomplished by the use of the circuit shown in Fig. 2. Its principal feature is that in

charging the current integrator, the potential of the target varies by about 2 V only, while the target assembly can be varied by ± 500 V with respect to ground.

The proton nuclear resonance frequency is determined by comparison with an A.N. frequency meter whose check points in turn were calibrated by com-

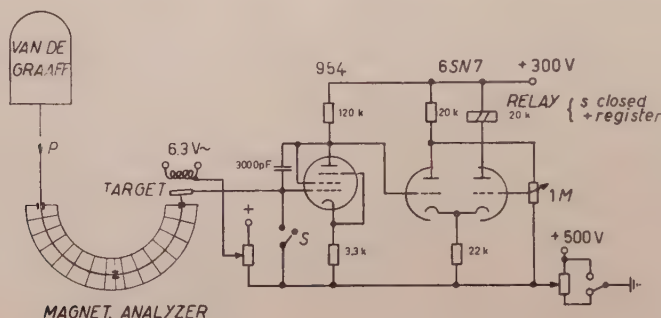


Fig. 2.

parison to the Swiss National broadcasting station ($\nu = (529 \pm 0.003)$ kHz). The distance of entrance and exit slits $L = (100.004 \pm 0.004)$ cm was measured by comparison with a S.I.P. standard meter calibrated by the Swiss National Bureau of standards.

3. - Energy and shape of observed resonance.

For the axial circular orbit passing through the centers of the spectrometer the relation between the value B of the magnetic field and the energy E of the deflected particle with the rest mass M_0 and the charge e is given by:

$$E = M_0 c^2 \left(\frac{1}{\sqrt{1 - \beta^2}} - 1 \right); \quad \frac{2 M_0 \beta}{L \sqrt{1 - \beta^2}} = \frac{e B}{c^2}; \quad E = \frac{(L e B)^2}{8 M_0 c^2} (1 - \delta),$$

where L is the distance of entrance and exit slits and $\delta = (L e B / 4 M_0 C^2)^2$ the relativistic correction to first order. The value of B is measured by the spin Larmor frequency of the proton: $\omega = \gamma_p B$ with γ_p the gyromagnetic ratio of the proton. If ν_c / ν_p is the ratio of the non-relativistic orbital to spin Larmor frequency of the proton in the same magnetic field, we have:

$$\frac{\nu_c}{\nu_p} = \frac{e}{\gamma_p M_0 c},$$

and hence:

$$E = \frac{L^2 \omega^2}{8} M_0 \left(\frac{\nu_c}{\nu_p} \right)^2 (1 - \delta),$$

expressing the energy in terms of the two measured quantities L and ω and the fundamental atomic constants M_0 and ν_c/ν_p . If one wishes to express the energy in the usual absolute eV scale one has:

$$V = \frac{Ec}{e} \cdot 10^{-8} = \frac{L^2 \omega^2 (1 - \delta)}{8 \gamma_p} \left(\frac{\nu_c}{\nu_p} \right) \cdot 10^{-8} \text{ abs. volt.}$$

The only two significant atomic constants ν_c/ν_p and γ_p have been determined very accurately and consistently by SOMMER, THOMAS and HIPPLE [9], and THOMAS, DRISCOLL and HIPPLE [10].

In order to ascertain the position of a resonance maximum accurately and to determine its breadth one has to measure the profile of the actual resonance curve. This profile will in general be modified compared to a Breit-Wigner resonance curve for either thick or thin targets, because of:

- a) Energy spread of the impinging protons caused by the finite geometric resolution of the spectrometer.
- b) Fluctuation with time of the magnetic field.
- c) Doppler effect of the target nuclei.

The geometric energy spread can easily be shown to give a very nearly triangular energy distribution $N_0(E - E_0)$ around the center value E_0 if one assumes that the entrance slit is uniformly illuminated by a nearly uniform spectrum and that the protons strike the plane of the slit nearly perpendicularly. The base of the triangular distribution is $\Delta E = 4E_0 s/L$ where s is the equal width of entrance and exit slits.

Fluctuations of the magnetic field caused by the finite stabilization of the nuclear resonance control were found to follow with good accuracy a Gaussian distribution with a mean square deviation of:

$$\sqrt{\overline{\Delta_f^2}} \simeq 75 \text{ eV.}$$

The Doppler effect of the target nuclei is likewise equivalent to a Gaussian energy distribution of the incoming protons. If \overline{E} is the kinetic energy of the protons in the laboratory system, the probability for a proton to have an

effective energy between E and $E+dE$ is [11]:

$$N(E) dE = \frac{1}{2} \sqrt{\frac{M_2}{M_1 \bar{E} k T_{\text{eff}} \pi}} \exp \left[-\frac{(E - \bar{E})^2 M_2}{4 M_1 \bar{E} k T_{\text{eff}}} \right] \cdot dE,$$

where M_1 and M_2 are the masses of incoming and target nucleus respectively and terms higher than $\sqrt{k T_{\text{eff}} / \bar{E}}$ are neglected. T_{eff} is the equivalent temperature of a Debye solid.

The effects b) and c) can therefore be combined to a single Gaussian:

$$N_G(E - \bar{E}) = \frac{1}{\Delta \sqrt{2\pi}} \exp \left[-\frac{(E - \bar{E})^2}{2\Delta^2} \right].$$

If now $\sigma(E - E^*)$ is the cross-section of the reaction with a resonance at $E = E^*$ the yield of reaction particles for protons with energies around the center value E_0 impinging on a target of thickness d is given by:

$$Y(\bar{E}_0) = \text{const} \int_0^\infty \left\{ \int_0^d \sigma(E^* - (E - Kx)) dx \int_0^\infty N_0(\bar{E} - E_0) \exp \left[-\frac{(E - \bar{E})^2}{2\Delta^2} \right] d\bar{E} \right\} dE,$$

where K is the energy loss of the protons per unit target thickness. For a single isolated resonance σ is given by the Breit-Wigner one level formula:

$$\sigma(E^* - E) = \frac{\sigma_0}{(E^* - E)^2 + \Gamma^2/4}.$$

In the case of thin targets the quantitative interpretation of the measurements is complicated by the necessity of determining the thickness d , which cannot be done directly by weighing of the target. Although d might be determined indirectly the procedure is further complicated by inhomogeneities of the target, which are particularly disturbing for very thin targets. Moreover the yield curves are modified by straggling, i.e. the statistical nature of the slowing down process producing an additional energy spread which increases with depth in the target.

4. - Results.

As an example of the determination of E^* we present in Figs. 3 and 4 our results for the 871 kV resonance of $^{19}\text{F}(p\alpha\gamma)^{16}\text{O}$ and the 991 kV resonance of $^{27}\text{Al}(p\gamma)^{28}\text{Si}$. The yields are plotted against the frequency ν of the controlling

proton spin resonance rather than in terms of energy. The solid curves are calculated with the three parameters E^* , I and d chosen for best fit.

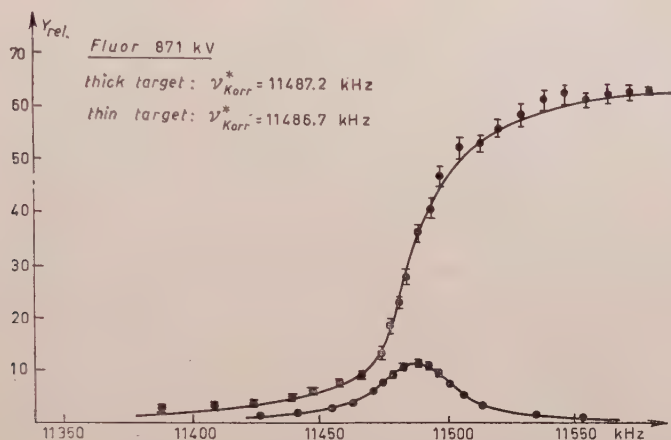


Fig. 3.

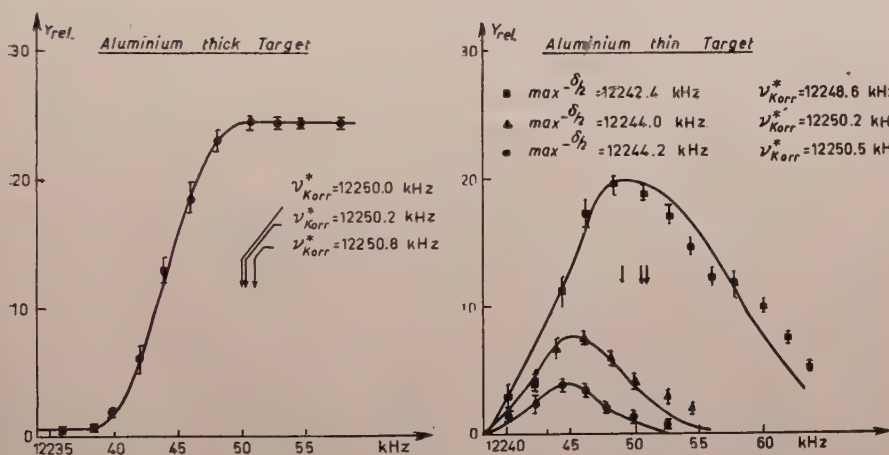


Fig. 4.

In the case of fluorine the frequency ν corresponding to the energy E^* of the resonance was found to be 11487.2 kHz for the thick target. For the thin target of thickness 9.0 kHz, ν is 11486.7 kHz. For aluminium the results of three independent runs on thick targets were: 12250.0, 12250.2, 12250.8 kHz and for the two thin targets of thickness 1.5 and 3 kHz respectively: 12250.5 and 12250.2 kHz. The complete set of results together with those of other workers is presented in Table I.

TABLE I.

	E^* (keV)	Γ (keV)
Lithium 441 keV		
FOWLER and LAURITSEN [15]	441.4 ± 0.5	12
HUNT [3]	441.5 ± 0.5	12.2 ± 0.5
Present work	441.2 ± 0.6	12 ± 1
Fluorine 340 keV		
MORRISH [2]	340.4 ± 0.4	3 ± 1
HUNT [3]	340.4 ± 0.4	2.9 ± 0.2
Present work	340.5 ± 0.3	3.3 ± 0.2
Fluorine 871 keV		
HERB, SNOWDON and SALA [1]	873.5 ± 0.9	
FAMULARO and PHILIPS [5]	872.5 ± 1.8	
HUNT and FIRTH [4]	874.5 ± 0.9	5.4 ± 0.3
Present work	871.3 ± 0.4	4.5 ± 0.2
Aluminium 991 keV		
HERB, SNOWDON and SALA [1]	993.3 ± 1	
BENDER, SHOEMAKER, KAUFMANN and BOURICIUS [14]		~ 0.1
Present work	990.8 ± 0.2	0.06 ± 0.03

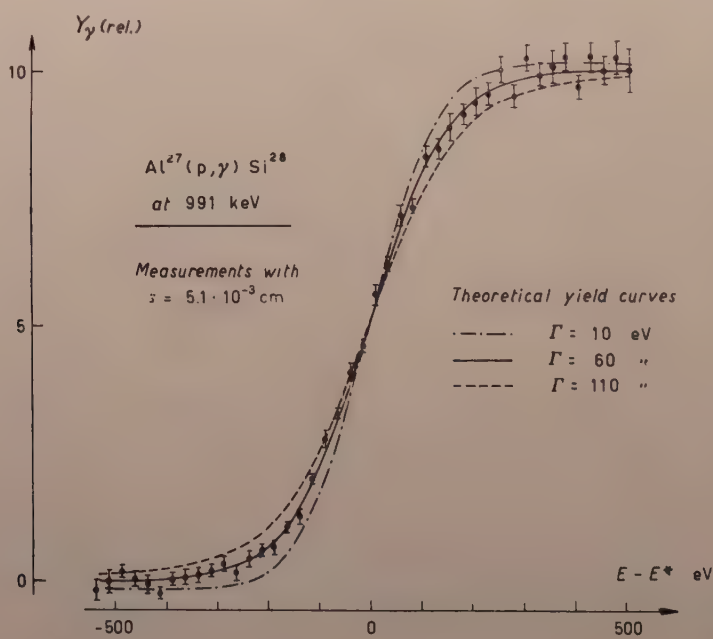


Fig. 5.

The determination of the breadth of the very narrow resonance of Al at 991 keV was done in the manner described above, keeping the field setting constant and varying the potential of the target. Only thick targets were used. As an example Fig. 5 shows the measurements for slit widths of $s = 0.005$ cm. The curves were computed for three different values of $I = 10, 60$ and 110 eV. The actual temperature of the target was $T = 170^\circ\text{C}$. From the Debye temperature of aluminium $\theta = 400^\circ\text{K}$ one obtains an effective temperature $T_{\text{eff}} = 470^\circ\text{K}$. From the combined measurements taken with slit widths $s = 0.003, 0.005, 0.007$ and 0.010 cm we conclude $I = (60 \pm 30)$ eV. The large uncertainty is mainly due to the fact that the shape of the yield curves is primarily determined by magnetic field variation and Doppler broadening.

5. - Discussion.

Table I shows that the present results are in excellent agreement with those of other workers for the lithium resonance at 441 keV and the fluorine resonance at 340 keV. However there is a noticeable discrepancy of our values for fluorine at 871 keV and for aluminium at 991 keV. The origin of this difference is not clear, it might be due to some systematic error in the electrostatic analyzer method. This belief is supported by a direct absolute measurement of the energy of the γ -ray emitted by ${}^7\text{Li}$ in the transition from the first excited to the ground state by MARMIER [12] who finds $E_\gamma = (477.3 \pm 0.3)$ keV. On the other hand this energy was determined by BROWN, SNYDER, FOWLER and LAURITSEN [13] by measuring the energy of protons inelastically scattered by lithium in an electrostatic and magnetic analyzer which were calibrated using the ${}^{19}\text{F}(p\alpha\gamma){}^{16}\text{O}$ resonance with $E^* = 873.5$ keV as standard. Their result is $E_\gamma = (479.0 \pm 1.0)$ keV. Assuming our value of 871.3 keV for the standard, the γ -ray energy would be reduced to (477.8 ± 1) keV, in excellent agreement with MARMIER's value.

From the measured width $I = (60 \pm 30)$ eV of the aluminium resonance at 991 keV we can now determine the width of this level without the effect of the Coulomb barrier. Let us assume that the level in ${}^{28}\text{Si}$ is a single particle level and that the single proton has orbital angular momentum zero. Taking the nuclear radius as $R = 1.4 \cdot 10^{-13} A^{\frac{1}{3}}$ cm one finds the Coulomb barrier penetrability $P_{0p} = 0.0016$ and hence the width $I_0 = I/P_{0p} = (38 \pm 20)$ keV.

REFERENCES

- [1] R. G. HERB, S. C. SNOWDON and O. SALA: *Phys. Rev.*, **75**, 246 (1949).
- [2] A. H. MORRISH: *Phys. Rev.*, **76**, 1651 (1949).
- [3] S. E. HUNT: *Proc. Phys. Soc.*, A **65**, 982 (1952).
- [4] S. E. HUNT and K. FIRTH: *Phys. Rev.*, **99**, 786 (1955).
- [5] K. F. FAMULARO and G. C. PHILIPS: *Phys. Rev.*, **91**, 1195 (1953).
- [6] W. E. SHOUPP, B. JENNINGS and W. JONES: *Phys. Rev.*, **76**, 502 (1949).
- [7] F. BUMILLER, H. H. STAUB and H. E. WEAVER: *Helv. Phys. Acta*, **29**, 83 (1956).
- [8] H. W. KNOEBEL and E. L. HAHN: *Rev. Sci. Inst.*, **22**, 904 (1951).
- [9] H. SOMMER, H. A. THOMAS and J. A. HIPPLE: *Phys. Rev.*, **82**, 697 (1951).
- [10] H. A. THOMAS, R. L. DRISCOLL and J. A. HIPPLE: *Phys. Rev.*, **78**, 787 (1950).
- [11] P. MORRISON and E. SEGRÈ: *Experimental Nuclear Physics*, (New York, 1953).
- [12] P. MARMIER in: AYZENBERG and LAURITSEN: *Rev. Mod. Phys.*, **27**, 87 (1955), Vol. 2.
- [13] A. B. BROWN, C. W. SNYDER, W. A. FOWLER and C. C. LAURITSEN: *Phys. Rev.*, **82**, 159 (1951).
- [14] R. G. BENDER, F. C. SHOEMAKER, S. G. KAUFMANN and G. M. B. BOURICIUS: *Phys. Rev.*, **76**, 273 (1949).
- [15] W. A. FOWLER and C. C. LAURITSEN: *Phys. Rev.*, **76**, 314 (1949).

Interference Effects of Bremsstrahlung and Pair Production in Crystals.

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It has been suggested by WILLIAMS [1] and more recently by LANDAU and POMERANČUK [2] that some kind of density effect will occur for bremsstrahlung and pair production in the ultrahigh energy region. Taking a single crystal as a target, there will be similarly an interference effect due to the regular array of the atoms, appearing at more moderate energies. This has been investigated in some theoretical papers [3], making use of the Weizsäcker-Williams method. The present report concerns a treatment of the problem by the Born approximation (*).

A simple estimate of the threshold energy of the effect is provided by the Weizsäcker-Williams method. In the rest system of the incoming electron, (considering now bremsstrahlung), a row of atoms passing the electron has its interatomic distances Lorentz-contracted to a/γ , where a is the lattice constant. Resolving the e.m. field of the passing atoms into equivalent photons, bremsstrahlung then appears as Compton scattering of these photons. Quanta with wavelengths of the order of the Compton wavelength $\lambda_c = \hbar/mc$, will be scattered predominantly. If now the contracted atomic spacing becomes comparable to λ_c , equivalent photons from different atoms will interfere constructively. It follows that the effect sets in at energies $\gamma \leq a/\lambda_c$, which is of order 500 MeV.

In Born approximation, the essential part of the bremsstrahlung and pair production matrix element is

$$(1) \quad \int V(\mathbf{r}) \exp[i\mathbf{q}\mathbf{r}] d\mathbf{r},$$

(*) A full version appeared in *Phys. Rev.*, **103**, 1055 (1956).

with V the atomic potential, and \mathbf{q} the atomic recoil momentum, multiplied by c and measured in units mc^2 ; all lengths are measured in units λ_c , and energies in units mc^2 . For a crystal target, we have to replace

$$(2) \quad V = \frac{Ze^2}{r} \exp[-\beta r] \rightarrow V = \sum_{\mathcal{L}} \frac{Ze^2 \exp[-\beta |\mathbf{r} + \mathcal{L} + \mathbf{u}_{\mathcal{L}}|]}{|\mathbf{r} + \mathcal{L} + \mathbf{u}_{\mathcal{L}}|},$$

where \mathcal{L} are all the lattice vectors, and $\mathbf{u}_{\mathcal{L}}$ the displacements of the atoms due to thermal vibrations of the lattice. Inserting into (1), one finds that the differential cross-section gets the factor

$$(3) \quad \left| \sum_{\mathcal{L}} \exp[i\mathbf{q}(\mathcal{L} + \mathbf{u}_{\mathcal{L}})] \right|^2.$$

The displacements $\mathbf{u}_{\mathcal{L}}$ can be expressed by the normal co-ordinates $a_t(\mathbf{q}')$ of the lattice [4], with \mathbf{q}' a vector of the fundamental Brillouin zone, t a polarization index. Then an average over the distribution of normal co-ordinates at a temperature T is performed, using the oscillator distribution function of BLOCH [5]. Further approximations include replacement of the Brillouin zone by a sphere, its radius connected to the Debye temperature Θ by

$$(4) \quad \omega_{\max} = k\Theta/\hbar,$$

and one obtains in the usual way [6]:

$$(5) \quad \begin{aligned} \langle \left| \sum_{\mathcal{L}} \exp[i\mathbf{q}(\mathcal{L} + \mathbf{u}_{\mathcal{L}})] \right|^2 \rangle = \\ = \exp[-Aq^2] \left| \sum_{\mathcal{L}} \exp[i\mathbf{q}\mathcal{L}] \right|^2 + N(1 - \exp[-Aq^2]), \end{aligned}$$

where N is the total number of atoms in the crystal; A is a function of T , given by [6]

$$(6) \quad A = \frac{3m^2c^2}{4Mk\Theta} \left[1 + 4 \frac{T}{\Theta} \Phi \left(\frac{\Theta}{T} \right) \right];$$

Φ is a tabulated function. The first term in (5) is a diffraction term; it consists of a Debye-Waller temperature factor $\exp[-Aq^2]$, and of a Laue-Bragg factor, which can be written for large crystals

$$(7) \quad \left| \sum_{\mathcal{L}} \exp[i\mathbf{q}\mathcal{L}] \right|^2 = \frac{(2\pi)^3}{\Delta} N \sum_{\mathbf{g}} \delta^3(\mathbf{q} - 2\pi\mathbf{g});$$

\mathbf{g} are all reciprocal lattice vectors, Δ the volume of a primitive lattice cell.

Therefore in this term, the recoil momentum \mathbf{q} is restricted to be a reciprocal lattice vector. The second term in (5) gives a Bethe-Heitler type contribution.

One can show that the Bethe-Heitler [7] bremsstrahlung matrix element in \mathbf{q} space is large only if \mathbf{q} is almost perpendicular to the direction of the primary electron, \mathbf{p}_1 . Consider momentum and energy conservation equations:

$$(8) \quad \mathbf{q} = \mathbf{p}_1 - \mathbf{p}_2 - \mathbf{k}, \quad \varepsilon_1 = \varepsilon_2 + k.$$

The minimum value of the recoil momentum is

$$(9) \quad \delta = p_1 - p_2 - k \approx \frac{k}{2\varepsilon_1 \varepsilon_2},$$

assuming all energies $\gg mc^2$. Take \mathbf{p}_1 as the Z axis; then

$$q_z = p_1 - p_2 \cos \vartheta_{e1} - k \cos \vartheta_{\gamma}.$$

As is well known, electron and γ -angle are of order $1/p_2$, $1/k$. Using $\varepsilon^2 = p^2 + 1$, and expanding for high energies and small angles, we obtain with the help of the second eq. (8):

$$(10) \quad q_z \sim \delta \sim 1/\varepsilon,$$

whereas $q_{\perp} \sim 1$. This proves our assertion.

The physical situation given by (7) and (10) is represented in Fig. (1), showing the pancake-shaped matrix element in the reciprocal lattice space. It is clear from this and from (10) that the effect will appear for $\delta \lesssim 2\pi/a$, which gives a threshold energy depending on the spectral component k . We can replace the point planes \approx perpendicular to \mathbf{p}_1 , (for small ϑ) by continuous planes, giving for (7):

$$(11) \quad \frac{2\pi}{a} N \sum_h \delta \left(\mathbf{q} \frac{\mathbf{a}_1}{a} - \frac{2\pi}{a} h \right),$$

\mathbf{a}_1 being a crystal axis and ϑ the angle between it and \mathbf{p}_1 .

To obtain the total cross-section, the Bethe-Heitler [7] formula has to be integrated over all directions of \mathbf{p}_2 and \mathbf{k} . We use the small-angle approxi-

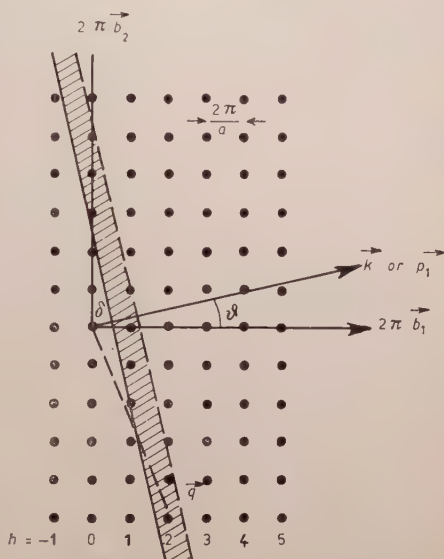


Fig. 1.

ation of this formula, and introduce the new variables $u = \theta_1 k$, $v = \theta_3 \varepsilon_2$, where $\theta_1 = \angle(\mathbf{p}_1, \mathbf{k})$, $\theta_3 = \angle(\mathbf{p}_1, \mathbf{p}_2)$. The essential azimuth variable of integration is $\psi = \angle(\mathbf{p}_1 \mathbf{p}_2 \text{ plane}, \mathbf{p}_1 \mathbf{k} \text{ plane})$; the other azimuth can be integrated out simply by the δ -function (11). The components of \mathbf{q} are in these variables

$$(12) \quad \begin{cases} q_{\perp}^2 = u^2 + v^2 + 2uv \cos \psi, \\ q_z = \delta + \frac{u^2}{2k} + \frac{v^2}{2\varepsilon_2}, \end{cases}$$

and we replace ψ by the new variable q_{\perp}^2 .

This gives for the total cross section

$$(13) \quad \sigma_t = N \sum_h \int' 2\pi\sigma_{BH} \frac{\partial(\theta_1\theta_3\psi)}{\partial(uvq_{\perp}^2)} du dv dq_{\perp}^2 \frac{2 \exp[-Aq^2]}{a[\partial^2 q_{\perp}^2 - (q_z - 2\pi h/a)^2]^{\frac{1}{2}}} + \\ + N \int 2\pi\sigma_{BH} (1 - \exp[-Aq^2]) d\theta_1 d\theta_3 d\psi;$$

the prime means integration only over a region of real square root. At $T=0$, the A 's for Cu and other elements are of order 100, and this allows some approximations before the integrations. These can then be carried out analytically, except a last one over q which has to be done numerically for each element separately, the functions depending on Z , ϑ , and the screening function $F(q)$ of Bethe [7]. The result is:

$$(14) \quad \sigma_t^{\text{Br}} = N \frac{Z^2}{137} \left(\frac{e^2}{mc^2} \right)^2 \frac{dk}{k\varepsilon_1^2} \left\{ (\varepsilon_1^2 + \varepsilon_2^2) \left[\Psi_1^c(\delta) + \Psi_1^0\left(\frac{\vartheta}{\delta}\right) + \sum_{h>0} \Psi_1^h(\delta, \vartheta) \right] - \right. \\ \left. - \frac{2}{3} \varepsilon_1 \varepsilon_2 \left[\Psi_2^c(\delta) + \Psi_2^0\left(\frac{\vartheta}{\delta}\right) + \sum_{h>0} \Psi_2^h(\delta, \vartheta) \right] \right\},$$

and similarly for pair production:

$$(14^1) \quad \sigma_t^{\text{P}} = N \frac{Z^2}{137} \left(\frac{e^2}{mc^2} \right)^2 \frac{d\varepsilon_+}{k^3} \left\{ (\varepsilon_+^2 + \varepsilon_-^2) \left[\Psi_1^c(\delta) + \Psi_1^0\left(\frac{\vartheta}{\delta}\right) + \sum_{h>0} \Psi_1^h(\delta, \vartheta) \right] + \right. \\ \left. + \frac{2}{3} \varepsilon_+ \varepsilon_- \left[\Psi_2^c(\delta) + \Psi_2^0\left(\frac{\vartheta}{\delta}\right) + \sum_{h>0} \Psi_2^h(\delta, \vartheta) \right] \right\}.$$

The square brackets replace the screening functions $\Phi_{12} - \frac{4}{3} \ln Z$ of BETHE [7]. Ψ_{12}^c comes from the second term in (5) and is independent of ϑ .

The functions Ψ are plotted vs. δ in Fig. 2 and 3 for copper at $T=0^\circ\text{K}$, together with the one-atom screening functions.

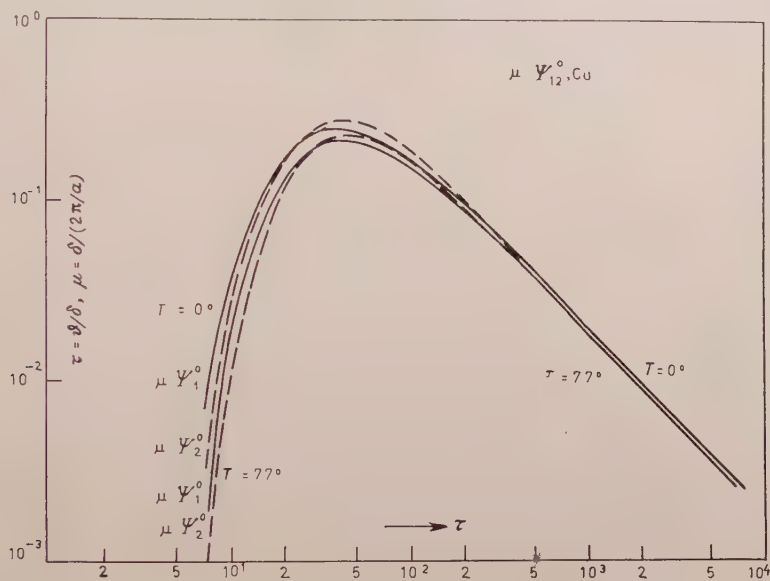


Fig. 2.

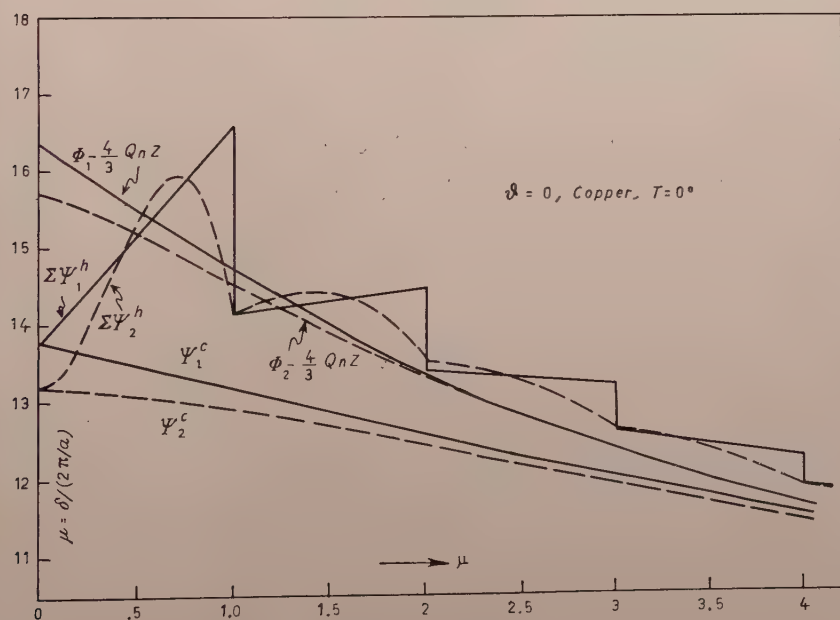


Fig. 3.

Using these curves, the bremsstrahlung spectrum is plotted in Fig. 4a for primary energy 1 GeV, and its ϑ dependence in Fig. 4b. Interference enhances the low end of the spectrum for angles ϑ of order $(a_{\text{screen}}/\lambda_c)(mc^2/E)$,

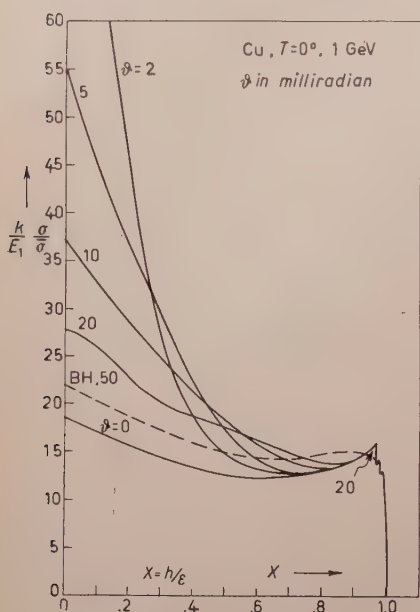


Fig. 4 a).

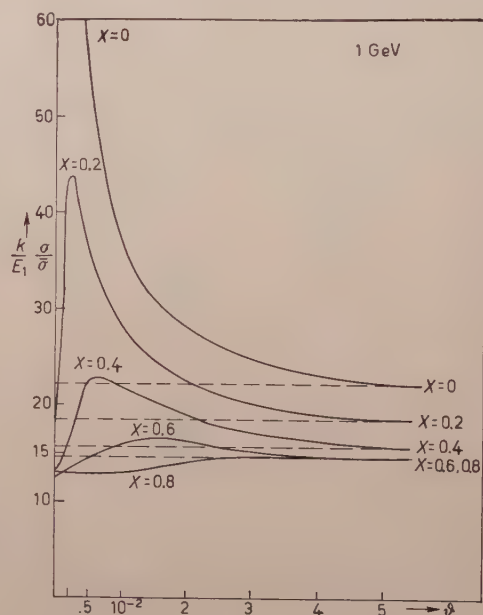


Fig. 4 b).

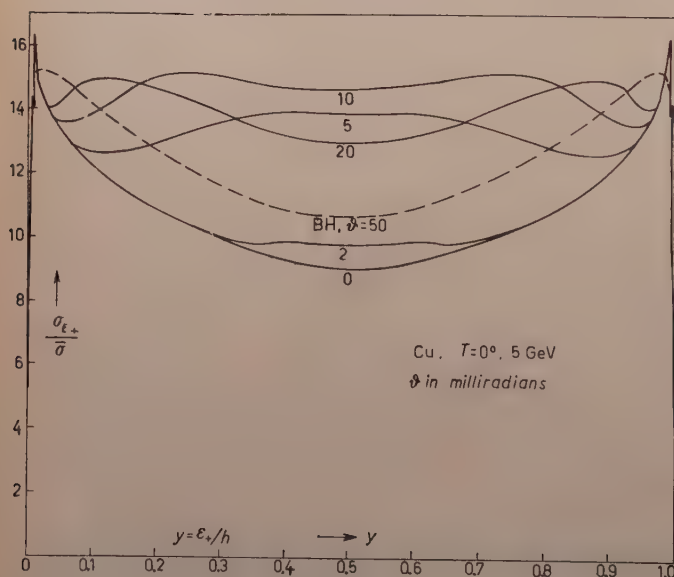


Fig. 5 a).

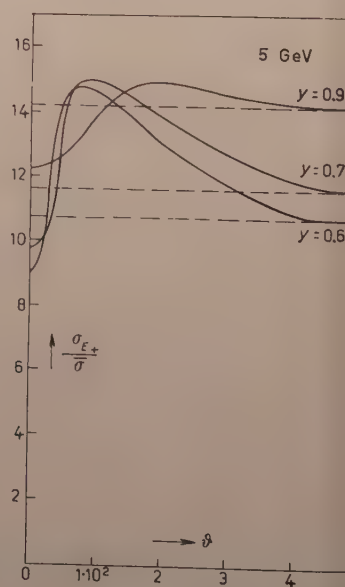


Fig. 5 b).

using the Thomas-Fermi screening radius $a_{\text{screen}}/\lambda_c = 137Z^{-\frac{1}{2}}$. Peaks at the high-frequency end are due to the harmonics in the Fourier decomposition of the potential.

The energy distribution for pair production is shown in Fig. 5a, b for a primary γ energy of 5 GeV. There is a similar enhancement for small angles.

REFERENCES

- [1] E. J. WILLIAMS: *Kgl. Danske Videnskab Selskab, Mat.-Fys. Medd.*, **13**, 4 (1935).
- [2] L. LANDAU and I. POMERANČUK: *Dokl. Akad. Nauk*, **92**, 535, 735 (1953); see also F. J. DYSON and H. ÜBERALL: *Phys. Rev.*, **99**, 604 (1955).
- [3] B. FERRETTI: *Nuovo Cimento*, **7**, 118 (1950); M. L. TER-MIKAEJAN: *Žu Eksper. Teor. Fiz.*, **25**, 296 (1953); E. M. PURCELL: unpublished.
- [4] F. SEITZ: *The Modern Theory of Solids* (New-York, 1940).
- [5] F. BLOCH: *Zeit. f. Phys.*, **74**, 295 (1932).
- [6] P. P. EWALD in H. GEIGER and K. SCHEEL: *Handbuch der Physik* (Berlin, 1933), Vol. **23**.
- [7] H. A. BETHE: *Proc. Cambridge Phil. Soc.*, **30**, 524 (1934).

PARTE SECONDA

SEZIONE SECONDA: Questioni teoriche.

The Vacuum in Quantum Electrodynamics.

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The theory of quantum electrodynamics has had a great deal of success, but involves some fundamental inconsistencies. People have concentrated their attention on the transitions produced by the interaction of the electrons and positrons with the electromagnetic field and have calculated various consequences of these transitions that can be compared with experiment. The calculations are made in terms of the interaction representation, in which only the interaction energy gives rise to changes in the wave function.

Now transitions are significant only if the states between which they occur are approximately stationary. This is not the case with quantum electrodynamics. Even the state that counts as the vacuum is far from being stationary. With this state, after the lapse of a short time there is a probability that an electron-positron pair will have appeared. This probability is proportional to the small number $e^2/\hbar c$ multiplied into a divergent integral, so it is infinite.

The present work is concerned with the problem of getting a better approximation to the vacuum state. For this purpose one must not use the interaction representation, but must keep to an ordinary Schrödinger representation in terms of dynamical variables that do not involve the time explicitly.

A certain class of simple states will be considered, and the best one of these, as an approximation to the vacuum state, will be picked out. It is such that, after the lapse of a short time, there is no probability for the appearance of an electron-positron pair, but only a probability for the simultaneous appearance of two pairs. This probability is proportional to $(e^2/\hbar c)^2$, again multiplied into a divergent integral.

The presence of a divergent integral here shows that the problem of the accurate representation of the vacuum state is still far from being solved. However, one may expect that the new approximation will be more suitable

in the usual one as a basis for calculations in quantum electrodynamics, because transitions involving the simultaneous appearance of two pairs are more remotely connected with observed effects.

The hamiltonian.

We shall deal with states at a given instant of time t . The dynamical variables needed to describe the states consist of various field quantities ξ_x at time t , where x , short for x_1, x_2, x_3 , denotes a general point of three-dimensional space. We shall use the notation

$$\xi_{xr} = -\xi_x^r = -\partial\xi_x/\partial x_r,$$

with $r = 1, 2, 3$. We shall take $c = 1, \hbar = 1$.

The variables that describe the electrons are the quantities ψ_{ar} and their conjugate complexes $\bar{\psi}_{ar}$, a being a spin suffix that takes on four values. They satisfy the anticommutation relations

$$\psi_{ax}\psi_{bx'} + \psi_{bx'}\psi_{ax} = 0, \quad \psi_{ax}\bar{\psi}_{bx'} + \bar{\psi}_{bx'}\psi_{ax} = \delta_{ab}\delta(x-x').$$

It is convenient to use a matrix notation in connection with these variables. Let ψ_{ax} for all a and x form a single-column matrix ψ and let $\bar{\psi}_{ax}$ for all a and x form a single-row matrix $\bar{\psi}$. Then if λ is a square matrix with elements $\lambda_{ax,bx'}$, the matrix $\bar{\psi}\lambda\psi$ has only a single element and is thus a simple quantity. We shall use the symbol $^+$ to denote the transpose of a matrix, so ψ^+ is a single-row matrix, $\bar{\psi}^+$ is a single-column matrix and $\psi^+\lambda\bar{\psi}^+$ is a single-element matrix. The relations (1) lead to

$$\bar{\psi}\lambda\psi + \psi^+\lambda^+\bar{\psi}^+ = \langle\lambda\rangle,$$

where $\langle\lambda\rangle$ denotes the diagonal sum of λ ,

$$\langle\lambda\rangle = \int \lambda_{ax,ax} d^3x,$$

summation over a being understood. We shall use the notation

$$\{\bar{\psi}\lambda\psi\} = \frac{1}{2}\bar{\psi}\lambda\psi - \frac{1}{2}\psi^+\lambda^+\bar{\psi}^+ = \bar{\psi}\lambda\psi - \frac{1}{2}\langle\lambda\rangle.$$

When $\langle\lambda\rangle$ is infinite, it will usually be that $\{\bar{\psi}\lambda\psi\}$ counts as a well-defined quantity while $\bar{\psi}\lambda\psi$ does not.

To avoid inessential complications in the theory, we shall take the form of electrodynamics with no scalar potential. The dynamical variables that describe the electromagnetic field are then the vector potential A_{rx} and the electric field E_{rx} . They are dynamical conjugates satisfying the commutation relation

$$(4) \quad [A_{rx}, E_{sx'}] = -\delta_{rs}\delta(x-x').$$

The Hamiltonian consists of four parts

$$(5) \quad H = H_e + H_i + H_{ph} + H_c.$$

H_e is the energy of the electrons alone and is in the matrix notation

$$(6) \quad H_e = \bar{\psi}(\alpha_r p_r + \alpha_m m)\psi.$$

The α 's here are λ -type matrixes with elements

$$\alpha_{ax\ bx'} =: \alpha_{ab}\delta(x-x'),$$

where α_{ab} denotes the elements of an ordinary spin matrix, and p_r is a λ -type matrix with elements

$$(p_r)_{ax\ bx'} = -i\delta_{ab}\delta^r(x-x').$$

H_i is the interaction energy and is in the matrix notation

$$(7) \quad H_i = e\bar{\psi}\alpha_r A_r \psi.$$

Here A_r is a λ -type matrix with elements

$$(A_r)_{ax\ bx'} = \delta_{ab}A_{rx}\delta(x-x').$$

H_{ph} is the energy of the photons and H_c is the energy of the Coulomb field. They are together equal to

$$(8) \quad H_{ph} + H_c = \int \left(\frac{1}{2} F_{rsx} F_{rsx} + \frac{1}{2} E_{rx} E_{rx} \right) d^3x,$$

where F_{rsx} is the magnetic field $A_{rsx} - A_{srx}$. To separate them we must separate the electromagnetic field into transverse and longitudinal parts.

Put

$$A_{rx} = \mathcal{A}_{rx} + V_x^r, \quad E_{rx} = \mathcal{E}_{rx} + U_x^r,$$

where $V_x{}^r$ and $U_x{}^r$ are the gradients of scalars V_x and U_x , and

$$\mathcal{A}_{rx}{}^r = 0, \quad \mathcal{E}_{rx}{}^r = 0.$$

thus

$$V_x{}^{rr} = A_{rx}{}^r, \quad U_x{}^{rr} = E_{rx}{}^r,$$

adding to

$$\begin{cases} V_x = -(4\pi)^{-1} \int |x - x'|^{-1} A_{rx'}{}^r d^3x', \\ U_x = -(4\pi)^{-1} \int |x - x'|^{-1} E_{rx'}{}^r d^3x'. \end{cases}$$

It is easily verified that the variables \mathcal{A}_{rx} , \mathcal{E}_{rx} that describe the transverse part of the field commute with the variables V_x , U_x that describe the longitudinal part of the field, and that

$$[V_x, E_{rx'}{}^{r'}] = \delta(x - x').$$

The electrical energy now separates into two parts

$$\frac{1}{2} \int E_{rx} E_{rx} d^3x = \frac{1}{2} \int \mathcal{E}_{rx} \mathcal{E}_{rx} d^3x + \frac{1}{2} \int U_x{}^r U_x{}^r d^3x.$$

The second of these is the Coulomb energy,

$$H_c = -\frac{1}{2} \int U_x{}^{rr} U_x d^3x = (8\pi)^{-1} \iint E_{rx}{}^r E_{sx'}{}^{s'} |x - x'|^{-1} d^3x d^3x'.$$

are left with

$$H_{ph} = \int \left(\frac{1}{4} F_{rsj} F_{rsj} + \frac{1}{2} \mathcal{E}_{rj} \mathcal{E}_{rj} \right) d^3x.$$

The Hamiltonian equations of motion must be used in conjunction with supplementary conditions, one for each point x ,

$$E_{rx}{}^r + e\{\bar{\psi} \varrho_x \psi\} \approx 0.$$

The density matrix ϱ_x here is a λ -type matrix with elements

$$(\varrho_x)_{ax'by''} = \delta_{ab} \delta(x - x') \delta(x' - x'').$$

2. - Creation and annihilation operators.

We may express the dynamical variables ψ and $\bar{\psi}$ in terms of creation and annihilation operators for electrons and positrons. Let $p_0 = (m^2 + p^2)^{\frac{1}{2}}$ and

$$(14) \quad \begin{cases} \bar{\eta} = \frac{1}{2}\{1 + (\alpha_r p_r + \alpha_m m)p_0^{-1}\}\psi \\ \zeta = \frac{1}{2}\{1 - (\alpha_r p_r + \alpha_m m)p_0^{-1}\}\psi. \end{cases}$$

Thus $\bar{\eta}$ and ζ are single-column matrices whose sum is $\bar{\psi}$. The conjugate complex equations are

$$(15) \quad \begin{cases} \eta = \frac{1}{2}\bar{\psi}\{1 + (\alpha_r p_r + \alpha_m m)p_0^{-1}\} \\ \bar{\zeta} = \frac{1}{2}\bar{\psi}\{1 - (\alpha_r p_r + \alpha_m m)p_0^{-1}\}. \end{cases}$$

η and $\bar{\zeta}$ are single-row matrices whose sum is $\bar{\psi}$.

To give a meaning to the p_0^{-1} in these equations we must express them in terms of the momentum representation. This involves working with matrix elements ψ_{av} of ψ , given by

$$(16) \quad \psi_{av} = (2\pi)^{-\frac{3}{2}} \int e^{-i(axp)} \psi_{av} d^3x.$$

Equations (14) and (15) then give us the matrix elements $\bar{\eta}_{av}$, ζ_{av} , η_{av} , $\bar{\zeta}_{av}$. They have the interpretation: η_{av} is the creation operator for an electron of momentum p , ζ_{av} is the creation operator for a positron of momentum $-p$, $\bar{\eta}_{av}$ and $\bar{\zeta}_{av}$ are the corresponding annihilation operators.

Their anticommutation relations are easily worked out. They are

$$(17) \quad \begin{cases} \bar{\eta}_{av}\eta_{bv'} + \eta_{bv'}\bar{\eta}_{av} = \frac{1}{2}\{1 + (\alpha_r p_r + \alpha_m m)p_0^{-1}\}_{ab}\delta(p - p') \\ \bar{\zeta}_{av}\zeta_{bv'} + \zeta_{bv'}\bar{\zeta}_{av} = \frac{1}{2}\{1 - (\alpha_r p_r + \alpha_m m)p_0^{-1}\}_{ba}\delta(p - p'), \end{cases}$$

and the other relations have zero on the right-hand side.

Equations (14) and (15) give

$$(18) \quad \eta p_0 \bar{\eta} = \frac{1}{2}\bar{\psi}(p_0 + \alpha_r p_r + \alpha_m m)\psi$$

$$(19) \quad \bar{\zeta} p_0 \zeta = \frac{1}{2}\bar{\psi}(p_0 - \alpha_r p_r - \alpha_m m)\psi.$$

Transposing the matrices in (19), we get

$$(20) \quad \begin{cases} \zeta^\dagger p_0 \bar{\zeta}^\dagger = \frac{1}{2}\psi^\dagger(p_0 - \alpha_r p_r - \alpha_m m)^\dagger \bar{\psi}^\dagger \\ \quad = -\frac{1}{2}\bar{\psi}(p_0 - \alpha_r p_r - \alpha_m m)\psi + \frac{1}{2}\langle p_{0m} \rangle. \end{cases}$$

from (2). Equations (18) and (20) give

$$(21) \quad H_0 = \eta p_0 \bar{\eta} + \zeta^\dagger p_0 \bar{\zeta}^\dagger - \frac{1}{2} \langle p_0 \rangle.$$

The last term here is an infinite constant and is due to the sea of negative-energy electrons.

We may express the transverse field variables \mathcal{A}_{rx} and \mathcal{E}_{rx} in terms of photon creation and annihilation operators. We put

$$(22) \quad \mathcal{A}_{rx} = \frac{1}{4} \pi^{-\frac{3}{2}} \int e^{-i(xk)} (\pi_{rk} + \bar{\pi}_{r-k}) d^3k / |k|,$$

$$(23) \quad \mathcal{E}_{rx} = -\frac{1}{4} i \pi^{-\frac{3}{2}} \int e^{-i(xk)} (\pi_{rk} - \bar{\pi}_{r-k}) d^3k.$$

The transverse character of \mathcal{A}_{rx} and \mathcal{E}_{rx} requires that

$$(24) \quad k_r \pi_{rk} = 0,$$

so that π_{rk} has only two independent components for each k value. These are the creation operators for a photon of momentum k , and their conjugate complexes are the annihilation operators.

The commutation relations of π_{rk} , $\bar{\pi}_{rk}$ are easily worked out. They are

$$(25) \quad [\pi_{rk}, \pi_{sk'}] = 0, \quad [\pi_{rk}, \bar{\pi}_{sk'}] = i k_{rs} |k| \delta(k - k'),$$

where

$$(26) \quad k_{rs} = \delta_{rs} - k_r k_s / k^2.$$

The k_{rs} factor in (25) is needed to secure consistency with (24).

Equations (22) and (23) make the expression (12) for the photon energy go over into

$$(27) \quad \left\{ \begin{aligned} H_{ph} &= \frac{1}{2} \int (\pi_{rk} \bar{\pi}_{rk} + \bar{\pi}_{rk} \pi_{rk}) d^3k, \\ &= \int \pi_{rk} \bar{\pi}_{rk} d^3k, \end{aligned} \right.$$

with neglect of an infinite constant of no importance.

We may put

$$(28) \quad \mathcal{A}_{rx} = \mathcal{A}_{rx}^+ + \mathcal{A}_{rx}^-,$$

where \mathcal{A}_{rx}^+ and \mathcal{A}_{rx}^- are the parts that refer to creation and annihilation of

photons respectively. Thus, for example

$$(29) \quad \mathcal{A}_{rz} = \frac{1}{4} \pi^{-\frac{3}{2}} \int e^{i(ak)} \bar{\pi}_{rk} d^3k / |k|.$$

3. — The representation of states.

The dynamical variables ψ_{ax} , $\bar{\psi}_{ax}$, A_{rx} , E_{rx} are operators operating to the right on vectors, called kets to distinguish them from other vectors, and written $|\rangle$. A ket that satisfies the supplementary conditions

$$(30) \quad (E_{rx} + e\{\bar{\psi}\partial_x\psi\})|\rangle = 0.$$

represents a physical state.

A state at time t is represented by a ket $|t\rangle$ depending on t according to the Schrödinger equation

$$(31) \quad i d|t\rangle/dt = H|t\rangle.$$

The vacuum state $|V\rangle$ is a stationary state and so must satisfy

$$(32) \quad H|V\rangle = C|V\rangle,$$

where C is a number.

In most work on quantum electrodynamics people transform the Hamiltonian to the interaction representation, which causes the terms H_e and H_{ph} to drop out from it. But this transformation involves the time t and is of no use for studying stationary states. We must therefore keep H as we now have it and try to solve (32) and (30).

To represent the kets we first define a suitable standard ket $|S\rangle$ by means of a number of linear conditions, say

$$\kappa_n |S\rangle = 0.$$

These conditions must be all consistent with one another and there must be sufficiently many to fix $|S\rangle$ completely, except for an arbitrary numerical factor. We then express any ket $|P\rangle$ as

$$(33) \quad |P\rangle = \Psi |S\rangle,$$

with Ψ some function of the dynamical variables. Ψ is not uniquely determined, unless we impose some restriction on the dynamical variables that occur

in it, because we can replace it by $\Psi + \sum_n a_n z_n$, with the a_n any functions of the dynamical variables.

In electrodynamics a convenient set of conditions for $|S\rangle$ are those that make it the vacuum state for the case $e = 0$, namely

$$(34) \quad \bar{\eta}_{ap} |S\rangle = 0 \quad \bar{\zeta}_{ap} |S\rangle = 0$$

$$(35) \quad \bar{\pi}_{rk} |S\rangle = 0 \quad E_{rx} |S\rangle = 0.$$

These conditions are consistent, since the z operators all commute or anti-commute, and they are sufficient, since all dynamical variables are expressible in terms of the z 's and their dynamical conjugates. Of course this $|S\rangle$ does not represent the actual vacuum state. It does not satisfy the supplementary conditions (30), so it does not represent a state at all.

We can now express any ket in the form (33) with Ψ a function only of those variables that do not vanish when applied to $|S\rangle$, namely

$$(36) \quad \Psi = \Psi(\eta_{ap}, \zeta_{ap}, \pi_{rk}, V_x).$$

We shall find it convenient to work with somewhat more general Ψ 's, namely

$$(37) \quad \Psi = \Psi(\psi_{ax}, \bar{\psi}_{ax}, \pi_{rk}, V_x).$$

We shall consider simple kets of the form

$$(38) \quad |Q\rangle = e^{\bar{\psi}\lambda\psi} |S\rangle.$$

In general, to give a meaning to such a ket one would have to expand the exponential and apply the successive terms to $|S\rangle$. For the λ -matrices that are interesting, this procedure will usually lead to infinities and so will not give us a well-defined ket $|Q\rangle$. In the next section, however, it will be shown that *provided the matrix elements of λ all commute with one another*, one can in many cases give a meaning to $|Q\rangle$ without expanding the exponential, so that $|Q\rangle$ can be considered as well-defined even though the expansion leads to infinities.

4. - Some theorems about matrices.

To save writing, in this section we shall replace the two suffixes a, x of ψ_{ax} by a single suffix A , which we assume takes on discrete values. Thus (1) becomes

$$\psi_A \psi_B + \psi_B \psi_A = 0, \quad \psi_A \bar{\psi}_B + \bar{\psi}_B \psi_A = \delta_{AB}.$$

We shall be concerned with theorems connecting the single-column matrix ψ , the single-row matrix $\bar{\psi}$ and square matrices λ , μ whose elements λ_{AB} , μ_{AB} commute with all ψ_C , $\bar{\psi}_C$ but may involve other non-commuting quantities.

Since $\bar{\psi}\lambda\psi$ is a single-element matrix or simple quantity, we can give a meaning to its product with any matrix, either on the left or on the right. Thus, for example, $(\bar{\psi}\lambda\psi)\psi$ has a meaning as a single-column matrix with elements $(\bar{\psi}\lambda\psi)\psi_A$, and $(\bar{\psi}\lambda\psi)\mu$ has a meaning as a square matrix with elements $(\bar{\psi}\lambda\psi)\mu_{AB}$.

Theorem 1.

$$i[\psi, \bar{\psi}\lambda\psi] = \lambda\psi.$$

Proof: The left-hand side is a single-column matrix with elements

$$\begin{aligned} i[\psi_A, \bar{\psi}\lambda\psi] &= \psi_A \bar{\psi}_B \lambda_{BC} \psi_C - \bar{\psi}_B \lambda_{BC} \psi_C \psi_A \\ &= (\psi_A \bar{\psi}_B + \bar{\psi}_B \psi_A) \lambda_{BC} \psi_C = \lambda_{AC} \psi_C. \end{aligned}$$

Theorem 2.

$$i[\bar{\psi}, \bar{\psi}\lambda\psi] = -\bar{\psi}\lambda.$$

Proof: Similar to theorem 1.

Theorem 3. If the elements of λ commute with the elements of μ , then

$$[\bar{\psi}\mu\psi, \bar{\psi}\lambda\psi] = \bar{\psi}[\mu, \lambda]\psi.$$

Proof: Since the elements of λ commute with those of μ ,

$$[\mu, \bar{\psi}\lambda\psi] = 0.$$

Hence

$$\begin{aligned} [\bar{\psi}\mu\psi, \bar{\psi}\lambda\psi] &= \bar{\psi}\mu[\psi, \bar{\psi}\lambda\psi] + [\bar{\psi}, \bar{\psi}\lambda\psi]\mu\psi \\ &= -i\bar{\psi}\mu\lambda\psi + i\bar{\psi}\lambda\mu\psi = \bar{\psi}[\mu, \lambda]\psi. \end{aligned}$$

Theorem 4. If the elements of λ commute with one another, then

$$e^{\bar{\psi}\lambda\psi}\psi e^{-\bar{\psi}\lambda\psi} = e^{-\lambda}\psi.$$

Proof: Introduce the single-column matrix R_θ defined by

$$R_\theta = e^{\theta\bar{\psi}\lambda\psi}\psi e^{-\theta\bar{\psi}\lambda\psi},$$

where θ is a number. Then

$$\begin{aligned} dR_\theta/d\theta &= e^{\theta\bar{\psi}\lambda\psi} \{(\bar{\psi}\lambda\psi)\psi - \psi(\bar{\psi}\lambda\psi)\} e^{-\theta\bar{\psi}\lambda\psi} \\ &= -e^{\theta\bar{\psi}\lambda\psi} \lambda \psi e^{-\theta\bar{\psi}\lambda\psi} \end{aligned}$$

from theorem 1. Since the elements of λ commute with one another, $\bar{\psi}\lambda\psi$ commutes with λ . Hence

$$dR_\theta/d\theta = -\lambda e^{\theta\bar{\psi}\lambda\psi} \psi e^{-\theta\bar{\psi}\lambda\psi} = -\lambda R_\theta.$$

The solution of this differential equation for R_θ with the initial condition $R_0 = \psi$ gives

$$R_\theta = e^{-\theta\lambda}\psi.$$

Equating the two expressions for R_θ and taking $\theta = 1$, we get the desired result.

Theorem 5. If the elements of λ commute with one another, then

$$e^{\bar{\psi}\lambda\psi}\bar{\psi}e^{-\bar{\psi}\lambda\psi} = \bar{\psi}e^\lambda.$$

Proof: Similar to theorem 4.

Theorem 6. If the elements of λ and μ all commute with one another, then

$$e^{\bar{\psi}\lambda\psi}\bar{\psi}\mu\psi e^{-\bar{\psi}\lambda\psi} = \bar{\psi}e^\lambda\mu e^{-\lambda}\psi.$$

Proof follows directly from theorems 4 and 5 and the fact that $\bar{\psi}\lambda\psi$ commutes with μ .

Suppose the elements of λ all commute with one another and let P be a single-element matrix that commutes with all ψ_A , $\bar{\psi}_A$ and such that $[P, \lambda_{AB}]$ commutes with λ_{CD} for all A, B, C, D . (These conditions could be realized, for example, by taking the λ_{AB} to be functions of some dynamical co-ordinates q and taking P to be a linear combination of the conjugate momenta p .) We can, of course, give a meaning to P multiplied on the left or on the right into any matrix. We now have

Theorem 7.

$$e^{\bar{\psi}\lambda\psi} P e^{-\bar{\psi}\lambda\psi} - P = \bar{\psi}(e^\lambda P e^{-\lambda} - P)\psi.$$

Proof: Introduce the single-element matrix S_θ defined by

$$S_\theta = e^{\theta\bar{\psi}\lambda\psi} P e^{-\theta\bar{\psi}\lambda\psi},$$

where θ is a number. Then

$$\begin{aligned} dS_\theta/d\theta &= e^{\theta\bar{\psi}\lambda\psi}(\bar{\psi}\lambda\psi P - P\bar{\psi}\lambda\psi)e^{-\theta\bar{\psi}\lambda\psi} \\ &= e^{\theta\bar{\psi}\lambda\psi}\bar{\psi}(\lambda P - P\lambda)\psi e^{-\theta\bar{\psi}\lambda\psi} \\ &= \bar{\psi}e^{\theta\lambda}(\lambda P - P\lambda)e^{-\theta\lambda}\psi \end{aligned}$$

from theorem 6. Thus

$$\frac{dS_\theta}{d\theta} = \frac{d}{d\theta} (\bar{\psi} e^{\theta\lambda} P e^{-\theta\lambda} \psi).$$

Integrating over the domain 0 to 1 for θ , we get the desired result.

The above theorems enable us in many cases to consider a ket $|Y\rangle$, given in terms of a known ket $|X\rangle$ by

$$(39) \quad |Y\rangle = e^{\bar{\psi}\lambda\psi} |X\rangle,$$

where the elements of λ all commute, as well-defined, even though one gets infinities if one expands the exponential. Suppose, for example, that one of the equations defining $|X\rangle$ is linear in ψ and $\bar{\psi}$ and is thus of the form

$$(a\psi + \bar{\psi}b)|X\rangle = 0,$$

where a and b are single-row and single-column matrices respectively whose elements commute with the elements of ψ and $\bar{\psi}$. Then we have

$$(40) \quad e^{\bar{\psi}\lambda\psi}(a\psi + \bar{\psi}b)e^{-\bar{\psi}\lambda\psi}|Y\rangle = 0.$$

If the elements of a and b commute with the elements of λ , this gives

$$(ae^{\bar{\psi}\lambda\psi}\psi e^{-\bar{\psi}\lambda\psi} + e^{\bar{\psi}\lambda\psi}\bar{\psi}e^{-\bar{\psi}\lambda\psi}b)|Y\rangle = 0.$$

From theorems 4 and 5 we now get

$$(41) \quad (ae^{-\lambda}\psi + \bar{\psi}e^{\lambda}b)|Y\rangle = 0,$$

which is an equation for $|Y\rangle$ free from infinities. If every one of the equations defining $|X\rangle$ leads by similar methods to an equation for $|Y\rangle$ that is free from infinities, then $|Y\rangle$ should be considered as well-defined.

We may repeat the process and set up

$$|Z\rangle = e^{\bar{\psi}\mu\psi}e^{\bar{\psi}\lambda\psi}|X\rangle,$$

provided the elements of μ and λ all commute with one another. The need to have the elements of μ commuting with the elements of λ arises because the elements of μ must commute with the elements of the coefficients of ψ and $\bar{\psi}$ in (41), just as the elements of λ must commute with the elements of the a and b of (40).

5. — First approximation to the vacuum state.

We may take the λ of the preceding section to be $-ieV$, since its elements $-ie\delta_{ab}V_x\delta(x-x')$ all commute with one another. We may take the P of theorem 7 to be $E_{rx}{}^r$ and then get

$$e^{-ie\bar{\psi}V\psi}E_{rx}{}^re^{ie\bar{\psi}V\psi} - E_{rx}{}^r = \bar{\psi}(e^{-ieV}E_{rx}{}^re^{ieV} - E_{rx}{}^r)\psi.$$

The commutation relation (10), written in terms of the λ -type matrix V , reads

$$(42) \quad [V, E_{rx}{}^r] = Q_x,$$

and so

$$[e^{-ieV}, E_{rx}{}^r] = -ieQ_x e^{-ieV}.$$

Hence

$$(43) \quad e^{-ie\bar{\psi}V\psi}E_{rx}{}^re^{ie\bar{\psi}V\psi} = E_{rx}{}^r + e\bar{\psi}Q_x\psi.$$

From (3)

$$e^{ie\{\bar{\psi}V\psi\}} = e^{ie\bar{\psi}V\psi}e^{-\frac{1}{2}ie\langle V \rangle},$$

and so

$$(44) \quad \begin{aligned} e^{-ie\{\bar{\psi}V\psi\}}E_{rx}{}^re^{ie\{\bar{\psi}V\psi\}} &= e^{\frac{1}{2}ie\langle V \rangle}(E_{rx}{}^r + e\bar{\psi}Q_x\psi)e^{-\frac{1}{2}ie\langle V \rangle} \\ &= E_{rx}{}^r - \frac{1}{2}e\langle Q_x \rangle + e\bar{\psi}Q_x\psi \\ &= E_{rx}{}^r + e\{\bar{\psi}Q_x\psi\}. \end{aligned}$$

The second of equations (35) now gives

$$(E_{rx}{}^r + e\{\bar{\psi}Q_x\psi\})e^{-ie\{\bar{\psi}V\psi\}}|S\rangle = 0.$$

Putting

$$(45) \quad |V_1\rangle = e^{-ie\{\bar{\psi}V\psi\}}|S\rangle,$$

we see that $|V_1\rangle$ satisfies the supplementary conditions (30) and so represents a physical state. It is the first approximation to the vacuum state.

For any dynamical variable ξ let

$$\xi^* = e^{ie\{\bar{\psi}V\psi\}}\xi e^{-ie\{\bar{\psi}V\psi\}}.$$

If ξ commutes with the elements of V , we may also write

$$\xi^* = e^{ie\bar{\psi}V\psi}\xi e^{-ie\bar{\psi}V\psi}.$$

We have

$$H|V_1\rangle = e^{-ie\{\bar{\psi}V\psi\}}H^*|S\rangle.$$

If $|V_1\rangle$ represented the vacuum state accurately, equation (32) would give

$$(46) \quad H^*|S\rangle = C|S\rangle.$$

We shall investigate the inaccuracy in this equation.

The elements of p_r commute with the elements of V , although the matrices themselves satisfy the commutation relation

$$(47) \quad [V, p_r] = V_r.$$

So we can apply theorem 6 and get

$$\begin{aligned} H_0^* &= e^{ie\bar{\psi}V\psi}(\alpha_r p_r + \alpha_m m)e^{-ie\bar{\psi}V\psi} \\ &= \bar{\psi}e^{ieV}(\alpha_r p_r + \alpha_m m)e^{-ieV}\psi \\ &= \bar{\psi}\{\alpha_r p_r - eV_r\} + \alpha_m m\psi. \end{aligned}$$

Hence

$$(48) \quad H_0^* + H_1^* = \bar{\psi}\{\alpha_r(p_r + e\mathcal{A}_r) + \alpha_m m\}\psi.$$

From (27)

$$(49) \quad H_{\text{ph}}^* = H_{\text{ph}} = \int \pi_{rk} \bar{\mathcal{L}}_{rk} d^3k.$$

Equation (44) leads to

$$(50) \quad E_{r,x}^* = E_{r,x} - e\{\bar{\psi}Q_x\psi\}.$$

Hence from (11)

$$(51) \quad H_0^* = (8\pi)^{-1} \iint (E_{rz}^* - e\{\bar{\psi}Q_x\psi\})(E_{sx'} - e\{\bar{\psi}Q_x\psi\})|x - x'|^{-1} d^3x d^3x'.$$

Collecting results, we get with the help of (21), (34) and (35)

$$(52) \quad H^* S = -\frac{1}{2} p_0 S - e \bar{\psi} \mathcal{A}_r \psi S - (8\pi)^{-1} e^2 \iint \{\bar{\psi} \mathcal{Q}_x \psi\} \{\bar{\psi} \mathcal{Q}_x \psi\} |x - x' + 1| d^3x d^3x' |S\rangle.$$

In the second and third terms here we may put $\psi = \bar{\eta} + \zeta$, $\bar{\psi} = \eta + \bar{\zeta}$ and then cancel some terms with the help of (34). The surviving terms show the inaccuracy in (46).

The main part of the inaccuracy comes from the second term in the right-hand side of (52). Its presence in the Schrödinger equation (31) gives rise to transitions in which an electron-positron pair is created, together with a photon, the transition probability being proportional to $e^2/\hbar c$.

It should be noted that (52) does not involve the longitudinal field variables W_x , U_x . The transformation from H to H^* is equivalent to the usual transformation for eliminating the longitudinal waves in quantum electrodynamics, and the ket $|V_1\rangle$ gives the approximation to the vacuum state that one uses after this elimination.

One can thus have confidence in the general method of using kets defined by equations like (39). The ket $|V_1\rangle$, although its defining equation (45) would have infinities if one expanded the exponential, is a well-defined thing because it has definite algebraic properties, and plays a fundamental role in the usual quantum electrodynamics.

B. - Second approximation to the vacuum state.

We shall consider a ket $|V_2\rangle$ of the form

$$(53) \quad |V_2\rangle = e^{-ie\{\bar{\psi}V\psi\}} e^{-\bar{\psi}\lambda\psi} |S\rangle,$$

where the elements of λ involve only the dynamical variables π_{rk} , not $\bar{\pi}_{rk}$. Thus the elements of λ satisfy the conditions of commuting with one another and with the elements of V , which conditions are necessary for $|V_2\rangle$ to be well-defined.

We have from (44)

$$(E_{rx}{}^r + e\{\bar{\psi}\mathcal{Q}_x\psi\}) |V_2\rangle = e^{-ie\{\bar{\psi}V\psi\}} E_{rx}{}^r e^{-\bar{\psi}\lambda\psi} |S\rangle = 0$$

since $E_{rx}{}^r$ commutes with the elements of λ . Thus $|V_2\rangle$ represents a physical state.

For any dynamical variable ξ let

$$\xi^{**} = e^{\bar{\psi}\lambda\psi} \xi^* e^{-\bar{\psi}\lambda\psi} = e^{\bar{\psi}\lambda\psi} e^{ie\{\bar{\psi}\nabla\psi\}} \xi e^{-ie\{\bar{\psi}\nabla\psi\}} e^{-\bar{\psi}\lambda\psi}.$$

Then

$$H|V_2\rangle = e^{-ie\{\bar{\psi}\nabla\psi\}} e^{-\bar{\psi}\lambda\psi} H^{**}|S\rangle.$$

We shall choose λ to make as many terms in $H^{**}|S\rangle$ as possible vanish, so that $|V_2\rangle$ will give the best approximation to the vacuum state.

With our present λ we can apply theorem 7 with $\bar{\pi}_{rk}$ for P and get

$$\begin{aligned} (54) \quad \bar{\pi}_{rk}^{**} &= e^{\bar{\psi}\lambda\psi} \bar{\pi}_{rk} e^{-\bar{\psi}\lambda\psi} = \bar{\pi}_{rk} + \bar{\psi}(e^{\lambda} \bar{\pi}_{rk} e^{-\lambda} - \bar{\pi}_{rk})\psi \\ &= \bar{\pi}_{rk} + \bar{\psi} e^{\lambda} (\partial e^{-\lambda} / \partial \pi_{sk}) \psi k_{rs} |k|, \end{aligned}$$

with the help of the commutation relations (25). From (48), (28) and (29)

$$H_0^* + H_1^* = \bar{\psi}\{\alpha_r(p_r + e\mathcal{A}_r^+) + \alpha_m m\}\psi + e' \int \bar{\psi} e^{i(xk)} \psi \bar{\pi}_{rk} d^3k / |k|,$$

where $e' = \frac{1}{4}e\pi^{-\frac{3}{2}}$ and x is conted as a λ -type matrix. Thus from theorem 6

$$H_0^{**} + H_1^{**} = \bar{\psi} e^{\lambda} \{\alpha_r(p_r + e\mathcal{A}_r^+) + \alpha_m m\} e^{-\lambda} \psi + e' \int \bar{\psi} e^{\lambda} e^{i(xk)} e^{-\lambda} \psi \bar{\pi}_{rk}^{**} d^3k / |k|.$$

From (49)

$$H_{ph}^{**} = \int \pi_{rk} \bar{\pi}_{rk}^{**} d^3k.$$

Theorem 3 shows that $\bar{\psi}\lambda\psi$ commutes with $\bar{\psi}\mathcal{Q}_x\psi$ and hence (51) gives

$$H_c^{**} = H_c^*.$$

Collecting results, we get

$$\begin{aligned} (55) \quad H^{**}|S\rangle &= \bar{\psi} e^{\lambda} \{\alpha_r(p_r + e\mathcal{A}_r^+) + \alpha_m m\} e^{-\lambda} \psi |S\rangle + e' \int (\bar{\psi} e^{\lambda} e^{i(xk)} e^{-\lambda} \psi) \cdot \\ &\quad \cdot \bar{\psi} e^{\lambda} (\partial e^{-\lambda} / \partial \pi_{sk}) \psi k_{rs} d^3k |S\rangle + \int \pi_{rk} \bar{\psi} e^{\lambda} (\partial e^{-\lambda} / \partial \pi_{sk}) \psi k_{rs} |k| d^3k |S\rangle + \\ &\quad + (8\pi)^{-1} e^2 \iint \{\bar{\psi} \mathcal{Q}_x \psi\} \{\bar{\psi} \mathcal{Q}_{x'} \psi\} |x - x'|^{-1} d^3x d^3x' |S\rangle. \end{aligned}$$

We now choose λ so that

$$(56) \quad e^{\lambda} \{\alpha_r(p_r + e\mathcal{A}_r^+) + \alpha_m m\} e^{-\lambda} + \int \pi_{rk} e^{\lambda} (\partial e^{-\lambda} / \partial \pi_{sk}) k_{rs} |k| d^3k = \alpha_r p_r + \alpha_m m.$$

This makes (55) reduce to

$$(57) \quad H^{**} |S\rangle = -\frac{1}{2} \rho_0 |S\rangle + e' \int (\bar{\psi} e^{\lambda} e^{i(\omega t)} e^{-\lambda} \psi) \bar{\psi} e^{\lambda} (\partial e^{-\lambda} / \partial \pi_{sk}) \psi k_{rs} d^3 k |S\rangle + \\ + (8\pi)^{-1} e^2 \iint \{\bar{\psi} \partial_x \psi\} \{\bar{\psi} \partial_{x'} \psi\} |x - x'|^{-1} d^3 x d^3 x' |S\rangle,$$

in which terms bilinear in ψ and $\bar{\psi}$ have disappeared.

Let us examine the equation (56) for λ . It is best considered as an equation for the unknown square matrix $e^{-\lambda}$. Suppose it is expressed in a representation with the momentum variables p_r and also $\alpha_r p_r + \alpha_m m$ diagonal, so that

$$(\alpha_r p_r + \alpha_m m)_{ap, bp'} = \delta_{ab} \delta(p - p') s_b p'_0,$$

where s_b equals 1 for two values of b and -1 for the other two. Then, on multiplying (56) by $e^{-\lambda}$ on the left, we get

$$(58) \quad \left[\{\alpha_r(p_r + e\mathcal{A}_r^+) + \alpha_m m\} e^{-\lambda} + \int \pi_{rk} (\partial e^{-\lambda} / \partial \pi_{sk}) k_{rs} |k| d^3 k \right]_{ap, bp'} = (e^{-\lambda})_{ap, bp'} s_b p'_0.$$

This equation resolves itself into a number of separate equations, one for each column of $e^{-\lambda}$. A column of $e^{-\lambda}$ is like a wave function for a single electron. Denoting it by φ , which means putting $(e^{-\lambda})_{ap, bp'} = \varphi_{ap}$ with the b and p' understood, we have

$$(59) \quad \{\alpha_r(p_r + e\mathcal{A}_r^+) + \alpha_m m - s_b p'_0\} \varphi + \int \pi_{rk} (\partial \varphi / \partial \pi_{sk}) k_{rs} |k| d^3 k = 0.$$

The solution of this equation for φ may be obtained in the form of a power series in the variables π_{rk} . It must satisfy the initial condition

$$(60) \quad \varphi_{ap} = \delta_{ab} \delta(p - p') \quad \text{for} \quad \pi_{rk} = 0.$$

To understand the significance of equation (59), let us first neglect the last term in it. It becomes just the wave equation for a single electron moving with the energy $s_b p'_0$ in a magnetic field, constant in time, described by the potentials \mathcal{A}_{rx}^+ . The potentials at different points all commute, so the wave equation is like that for an electron moving in a given field and its solution involves no infinities. The potentials are complex, so the wave equation does not represent an actual physical problem, but its solution in the form of a power series in the variables π_{rk} will appear the same whether the potentials are real or complex. The condition (60) shows that the solution we need is just the wave function which gives the scattering by the magnetic field of incident electrons with momentum p'_r and energy $s_b p'_0$.

To see the effect of the last term in (59), let us solve the equation to the accuracy of terms linear in π_{rk} . Put

$$\varphi_{av} = \delta_{ab}\delta(p-p') + \int \tilde{z}_{av, rk} \pi_{rk} d^3k,$$

in which the $\tilde{z}_{av, rk}$ are unknown coefficients depending on the understood suffixes b and p' . Substituting in (59) and neglecting higher powers of π_{rk} than the first, we get

$$(61) \quad (\alpha_r p_r + \alpha_m m - s_b p'_0)_{ac} \int \tilde{z}_{cv, rk} \pi_{rk} d^3k + e(\alpha_r \mathcal{A}_r^+)_{ab, bp'} + \int \pi_{rk} \tilde{z}_{av, sk} k_{rs} |k| d^3k = 0.$$

We may assume $k_s \tilde{z}_{av, sk} = 0$, so that from (26)

$$k_{rs} \tilde{z}_{av, sk} = \tilde{z}_{av, rk}.$$

We have

$$\left\{ \begin{aligned} (\mathcal{A}_r^+)_{vv'} &= (2\pi)^{-3} \int \mathcal{A}_{rs}^+ e^{-i(x, v-p')} d^3x \\ &= \frac{1}{4} \pi^{-\frac{3}{2}} |p-p'|^{-1} \pi_{r(v'-v)}. \end{aligned} \right.$$

Thus, taking out the coefficient of π_{rk} in (61), we get

$$(62) \quad (\alpha_r p_r + \alpha_m m - s_b p'_0 + |k|)_{ac} \tilde{z}_{cv, rk} + e'(\alpha_r)_{ab} |k|^{-1} \delta(k-p'+p) = 0.$$

This equation determines the $\tilde{z}_{av, rk}$.

The last term in (59) gives rise to the term with $|k|$ in the coefficient of $\tilde{z}_{av, rk}$ and shows that the scattered waves in φ that are associated with the creation of a photon of energy $|k|$ satisfy a wave equation corresponding to a loss of energy of amount $|k|$. This shows the way in which the quantization of the field influences the solution of (59).

7. - Discussion.

The ket $|V_2\rangle$ obtained in the preceding section is probably the best ket to represent the vacuum that can be obtained by means of operators like $e^{\bar{v}A\psi}$ applied to $|S\rangle$. When H is applied to $|V_2\rangle$ the non-constant terms all contain e^2 as a factor. Such terms will presumably be less troublesome than the terms containing e which occur with the usual vacuum ket $|V_1\rangle$.

These e^2 terms give rise to transitions involving the simultaneous creation of two electron-positron pairs. The transition probability is proportional to

$(e^2/\hbar c)^2$, but still involves a divergent integral. Thus the infinities associated with the vacuum state are not eliminated by the present theory, but only removed a stage.

Besides having the improved ket $|V_2\rangle$ to represent the vacuum we have improved kets to represent other stationary states, e.g. $\pi_{rk}|V_2\rangle$ to represent the one-photon state and

$$(63) \quad e^{-ie\{\bar{\psi}\gamma\psi\}} e^{-\bar{\psi}\lambda\psi} \eta_{a\sigma} |S\rangle$$

to represent the one-electron state. The latter ket satisfies the supplementary conditions (30) and so represents a real electron with its Coulomb field, not a bare electron. (See P. A. M. DIRAC: *Can. Journ. Phys.*, **33**, 650 (1955)). It also represents in the first approximation any photon associated with the motion of the electron, since the errors in it are all of order e^2 .

The present work leaves a number of problems for further investigation. In the first place there is the question whether $|V_2\rangle$ is relativistic. The field equations of quantum electrodynamics, from which the Hamiltonian formalism is derived, are relativistic, so one would expect that a solution of these equations that represents the vacuum to a certain degree of accuracy would also be relativistic. But still it would be desirable to check directly whether $|V_2\rangle$ remains invariant under Lorentz transformations.

Secondly there is the question whether $|V_2\rangle$, which is an approximate eigenket of H , belongs to the minimum eigenvalue of H . $|V_2\rangle$ is the result of a transformation applied to $|S\rangle$ and the latter is obviously the state of lowest energy in the case of no interaction, $e = 0$, but this is not sufficient to ensure that $|V_2\rangle$ approximates to the state of lowest energy for $e \neq 0$. In the classical theory one can have a very large negative interaction energy between an electron and the field, leading to the phenomenon of a runaway electron. There may be some corresponding way in quantum theory of getting a negative interaction energy between the sea of negative-energy electrons and the field, which might lower the total energy considerably.

Finally, there is the main problem of getting an accurate expression for the vacuum ket. There are two ways in which one might attack it. The obvious way is just to work with more complicated kinds of kets and try to find one that fits. Alternatively, one might try to modify the Hamiltonian to make it have a ket of the kind we have been dealing with as an accurate eigenket. Probably it would not be difficult to make such a modification in H without disturbing the agreement of the theory with experiment, because the troublesome terms in H are not closely connected with observable effects, but it will be difficult to make such a modification relativistically.

The Universal Constant Limiting the Validity of the Quantized Field Theories.

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The suggestion that the quantum field theories are limited by a universal length has first been made by HEISENBERG [1]. Interest in the question has been renewed recently for the following reasons. (i) It has been made probable that quantum-electrodynamics, after charge renormalization, is mathematically inconsistent [2], quite apart from the fact, that it has been proved that at least one of the renormalization constants is infinite (which in itself constitutes a severe objection). To remove the (probable) inconsistency an upper limit for virtual momenta of the order [3]

$$(1) \qquad K \sim mce^{137}$$

has been suggested. (ii) The failure of meson theory, in any of its varieties, to yield quantitatively correct results strongly suggests that some fundamental physical changes have to be made. The renormalizable version (γ_5 -coupling; renormalizable only after an ad hoc and infinite addition to remove the infinite meson-meson scattering) contradicts the meson-nucleon scattering at low energies, and the version which at least qualitatively agrees with the meson-nucleon scattering (gradient-coupling) is not renormalizable (in the sense of the perturbation expansion). Furthermore, of course, the existence of K-mesons and hyperons, which cannot be understood on the basis of the present meson theory suggests that some physical change at some fundamental point is required.

If the validity of the present field theories is to be limited this can be conveniently described by an invariant cut-off, which limits the values of the virtual momenta at high energies [4]. It is true that in this way no consistent theory arises but it may be supposed that the cut-off constant will give an

indication as to the point where essential changes in the theory will occur. In the case of quantum-electrodynamics it may be supposed that the future correct theory will essentially (i.e. in very good approximation) reduce to the present theory with the cut-off introduced. If the present difficulties are due to an unknown new fundamental and general principle it may be conjectured that the cut-off to be introduced is *universal* and valid for all field theories. It is this assumption which will be tested in the following.

The unsatisfactory state of meson theory suggests that the cut-off constant is much smaller than the—very high—limit (1). (1) is indeed an upper limit. If quantum-electrodynamics in its present form contains a great measure of truth, after introduction of the cut-off, some physical reality must be attributed to the self-energies of the particles, now made finite by the cut-off. Thus we take the view that both the theoretical and the experimental masses are observable. To obtain the cut-off value the mass difference of π^\pm and π^0 lends itself most conveniently [5]. It is very probable that this is mostly due to the electromagnetic self-energy because the mesonic self-energy is likely to be the same for both particles owing to charge symmetry. In this case the mass difference is relatively large because of the quadratic divergence of the self-energy. Equating the mass difference with the electromagnetic self-energy we obtain a cut-off value for the momentum of the virtual particles of approximately

$$(2) \quad K \sim 4.4\mu c = 0.65 Mc,$$

where μ is the meson mass, M the nucleon mass. The value of K refers to a meson at rest (i.e. the centre of gravity of the bare meson and its virtual quanta is at rest). For a moving particle the cut-off momentum is obtained from the demand that

$$z^2 = \frac{1}{\mu^2 c^2} \{ (\sqrt{\mu^2 c^2 + (\mathbf{p} - \mathbf{K})^2} + K)^2 - p^2 \}$$

is invariant.

Unfortunately there is no other pair of particles from which the value of K could be determined directly. The proton-neutron mass difference cannot be due to electromagnetic causes alone (wrong sign), presumably it is due to mixed electromagnetic-meson causes. In this connection it is satisfactory that the purely electromagnetic self-energy of the proton (with the above cut-off) is only a few electron masses which can well be overcompensated by other causes.

On the other hand, a value of K has been derived from meson theory in the non relativistic limit [6]. In this limit a cut-off is essentially equivalent

to a finite source and the extension of the source is the reciprocal of K . If, with such a model, at least reasonable agreement with the experiments is to be achieved (for example for meson-nucleon scattering) the extension of the source must be of the order of magnitude \hbar/Mc , in agreement with the above figure. The very fact that two such entirely different data—an electromagnetic self energy and meson-nucleon scattering—lead to the same cut-off, is a strong argument in favour of the universal character of the limit K .

The fact that K turns out to be of the order of the nucleon mass is very satisfactory indeed. In the first place, it is rather plausible to suppose that fundamental changes in our very concepts of space and length (and therefore also in all field theories) will be required at the smallest length that can be measured by *physical* means. This is indeed the Compton wave length of the heaviest existing non-composite particle, i. e. of the nucleon, (the hyperons should be regarded as excited nucleons and can certainly not be used for a more accurate definition of length). No length can be measured to a greater accuracy than \hbar/Mc .

In the second place a change of theory for momenta larger than (2) explains why meson theory has met with little quantitative success. A cut-off of the order (2) does not leave a large range of validity for the present theory and the changes due to the cut-off and the unknown features from the region beyond the cut-off will be of the same order of magnitude as what follows from the region where the present theory is (more or less) valid.

In contrast to meson theory, for quantum-electrodynamics the cut-off is so high that its influence is exceedingly small. In fact it turns out, that none of the well known results of quantum-electrodynamics are changed appreciably. The changes are smaller by several orders of magnitude than the accuracy to which the effects are established. For example, the magnetic moment of the electron is known (theoretically and experimentally) to 4 decimals whereas the cut-off would influence it only in the seventh decimal. The departure from the Klein-Nishina formula (in the rest-system) would only begin at 10^6 MeV. The change in the cross section for bremsstrahlung is altogether negligible except for photons whose energy is practically equal to the primary energy of the electron, and this is an uninteresting case.

Thus it can be concluded that the hypothesis of an universal limit of validity of present field theories given by an universal momentum Mc or an universal length \hbar/Mc is consistent with our present knowledge. It may be remarked though, that no new constant is really introduced but a new and more fundamental role is attributed to a constant (M) already known.

REFERENCES

- [1] W. HEISENBERG: *Ann. Phys.*, **5**, 20 (1938).
- [2] G. KÄLLÉN and W. PAULI: *Det Dansk. Vid. Selsk., Bohr number* (1955).
- [3] L. LANDAU: *Niels Bohr and the development of Physics* (London 1955).
- [4] E. ARNOUS and W. HEITLER: *Nuovo Cimento*, **2**, 1282 (1955).
- [5] R. P. FEYNMAN and G. SPEISMAN: *Phys. Rev.*, **94**, 500 (1954).
- [6] G. F. CHEW: *Phys. Rev.*, **94**, 1748, 1755 (1954); **95**, 1669 (1954).

Some Remarks on General Relativity and the Divergence Problem of Quantum Field Theory (*).

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The subject of the following lecture is nearly related to those of the foregoing lectures by professors HEITLER and DIRAC, but the point of view is different from theirs although not necessarily contradictory. At its best it is only a sketch of a program towards the development of which very little has been done so far.

In his lecture of this morning professor DIRAC could not use strong enough words to tell us how bad the present theory of quantum electrodynamics is. Although there can of course be no disagreement regarding facts, I would use a rather different language and say that the theory is astonishingly good and that this is mainly due to the circumstance that Diracs theory of negative and positive electrons on which it is based is essentially more realistic than the earlier attempts towards a relativistic formulation of quantum dynamics. The astonishingly wide range of the theory was already suggested by WEISSKOPF's result regarding the self energy of the electron with its weak, logarithmic divergence and became apparent through the new, invariant procedure of calculating observable quantities from the theory developed by TOMONAGA, SCHWINGER, FEYNMAN and their followers. With this in view I would tentatively take the standpoint that what is needed to overcome the present difficulties of quantum theory is not a new procedure of quantization but rather a still more realistic field theory fulfilling still stronger claims of invariance than those with respect to Lorentz and gauge transformations.

(*) Originally this lecture was called «Problems related to the big and small numbers of Physics», my intention having been to include some further considerations concerning the world at large. As it was actually delivered, however, the above title is more adequate.

As the first step towards the development of such a program I would regard the fulfilment of the claim of general relativistic invariance, meaning the introduction of the gravitational field quantities into the basic Lagrangian density of quantum electrodynamics adding to this the Lagrangian density of the pure gravitational field.

Now, the combination of quantum theory and gravitation is known to define a small length of subnuclear dimensions. This small length l_0 properly defined, we may use it as a natural unit of length taking $\hbar/l_0 c$ as the mass unit and $\sqrt{\hbar c}$ as the unit of electric charge. The arbitrary factors appearing in the definition of l_0 we shall choose so as to make the total Lagrangian density just mentioned when written in « natural units » as simple as possible, which leads to

$$l_0 = \sqrt{\frac{8\gamma\hbar}{c^3}} \approx 10^{-32} \text{ cm},$$

where γ is the ordinary gravitational constant. This may be expressed by adding the convention $2\kappa = 1$ ($\kappa = 8\pi\gamma/c^4$ being the Einstein gravitational constant) to the usual conventions $\hbar = 1$, $c = 1$.

As well known, general relativity seems to require a limitation of the amount of mass which may be concentrated within a sphere of given diameter d , this mass being subject to the inequality

$$M < \frac{c^2}{4\gamma} d.$$

In fact, for a larger mass value the gravitational field outside of the mass will exhibit the characteristic Schwarzschild singularity. Let us now apply this inequality to a wave packet of diameter d corresponding to a particle or quantum governed by a linear wave equation as long as gravitation is neglected. If the diameter d is small compared with the Compton wave length of the particle the energy will be of the order of magnitude $\hbar c/d$ and the mass inside the sphere in question thus $\sim \hbar/cd$. The inequality in question gives therefore

$$d > \frac{l_0}{\sqrt{2}},$$

according to which l_0 would appear to be a natural limit to the linear dimensions of the region within which a particle could be confined.

Although not a proof the above consideration would seem to give a certain basis to the belief that the inclusion of gravitation in quantum electrodynamics would rid the theory of the divergence difficulties [1].

Dr. S. DESER (who had already started an attempt to prove the non-singularity of quantum field theory when gravitation is included) and I have lately tried to regard the question from the point of view of the functional integration method developed by Feynman. This method in the form given by MATHEWS and SALAM has recently been applied by B. LAURENT to the gravitational interaction of two Dirac particles, whereby the well known difficulties of quantizing the gravitational field (connected with the subsidiary conditions) would seem to disappear [2]. The expression for the propagator corresponding to that which is decisive for the infinities of ordinary quantum electrodynamics would in the mentioned treatment take the form of a functional integral taken over all possible values in all points of space-time of the quantities defining the four-dimensional metrics of general relativity theory. Since the light cone depends on these quantities, this would imply a kind of average over mathematical poles differently situated. Although still no proof this consideration would again give an indication of the disappearance of the infinities when gravitation is taken into account and would seem to give mathematical expression to an idea mentioned by PAULI, at the Bern relativity congress of 1955 [3].

At this point Dr. DESER and I began to consider more seriously the question of the compatibility of the suggested result with the general well known theorem given by KÄLLÉN and LEHMANN, according to which under very general conditions the infinities in a system of interacting particles could not be weaker than for the corresponding free particles. Now, this theorem is essentially based on the validity of the energy-momentum principle in the usual form, i.e. the validity of the following relation

$$i \frac{\partial \varphi}{\partial x^\mu} = [\varphi, P_\mu],$$

where x^1, x^2, x^3, x^4 are space-time co-ordinates, P_1, P_2, P_3, P_4 energy-momentum components and φ any quantity belonging to the system. The proof of the theorem implies that according to the relation just mentioned not only the position of the centre of gravity in space and time of the system but also that of any individual particle belonging to it may be fixed with any desired degree of precision. Now, already from the above considerations it is very improbable that such a fixation is possible when general relativity is taken into account. Moreover, it is seen that the above equation is not consistent with general relativistic invariance. Thus the definition of the vector P_μ implies that at large distances from the system the co-ordinate system should asymptotically go over into an ordinary Lorentz frame, the P_μ being space integrals taken over the whole system. While the P_μ transform as vector components when the outer co-ordinate frame undergoes a Lorentz transformation they are in-

variants against an arbitrary transformation of the inner co-ordinates only. As is immediately seen these transformation properties are inconsistent with the above relation.

That this must be so is also clear from the fact that the P_μ are operators for a translation of the entire system within the outward Lorentz frame and that such a translation has no simple connection to the curvilinear co-ordinates used for the description of the inner part of the system. In this connection it should also be remembered that in general relativity theory there is no invariant way to separate the energy-momentum belonging to the gravitational field from the «material» energy-momentum of the system.

It is clear that quantum electrodynamics including gravitation is only a very special and idealized case of a realistic quantum theory, which ought to include nucleons and mesons of all possible kinds as well. I shall not enter here on the difficult problem of the proper extension of the point of view of general relativistic invariance so as to include also the fields corresponding to these particles, which is also the problem of finding an adequate formulation of Yukawa's fruitful idea regarding the connection between nuclear forces and mesons. I shall finish this lecture with a small remark concerning the problems of the world at large i.e. the so-called cosmological problems. Here the typist of the first edition of the congress program has expressed my viewpoint somewhat more strongly than I would have done myself by changing the word big in the title of my lecture into bug. Thus I have tried to argue in favour of a program according to which the problems in question have hardly any closer relation to the entire universe than those of ordinary astrophysics, the question being rather to describe the state and evolution of our system of galaxies in a similar way as is attempted for other stellar systems such as the galaxies themselves.

In this way it seems possible to interpret the famous Eddington relations between «cosmological» and atomic quantities by means of the ordinary physical laws, giving indications as to the state of the metagalactic system in a certain phase of its evolution rather than to the existence of hitherto unknown laws of nature.

REFERENCES

- [1] A remark by L. LANDAU [*Niels Bohr and the development of physics* (London, 1955), p. 60] seems to show that he has been led to consider a momentum corresponding to l_0 as an automatic cut off limit due to gravitation in quantum electrodynamics.

- [2] B. LAURENT: *Nuovo Cimento* (soon to appear). Professor J. WHEELER has kindly told us that the problem of the quantization of the gravitational field has recently been attacked by C. MISNER, who has been able to overcome certain remaining difficulties of uniqueness by a suitable choice of the integration variables.
- [3] W. PAULI: *Bern Congress on Relativity Theory*, 1955.

Non-Linear Generalizations of the Field Theory and the Constant of Minimal Length.

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The congress on fundamental constants honouring the memory of AVOGADRO gives occasion not only to review habitual physical constants, but also to analyze the values of new important constants representing the strength of the interaction between nucleons and mesons and even to discuss such new possible constants as the constant of non-linear self-interaction and the constant of minimal universal length. We may point out some results pertaining to the last mentioned problems.

1. — Non-linear generalizations of the field equations proposed in a somewhat arbitrary manner by MIE and BORN-INFELD in the electromagnetic case have been found to be a necessary consequence of the relativistic quantum field theory (HEISENBERG, EULER, KOCKEL, DELBRÜCK). Speaking in an « anschaulicher » manner non-linearities arise through the mutual transmutations of particles. We may call such non-linearities as of vacuum or induced type (class B), distinguishing them from some primordial, genuine non-linearities, which can possibly be present in equations, independently from any interaction (class A).

The best known case of non-linear equations are the Einstein equations of the gravitational field (class A). But starting from the linear equations of the weak gravitational field we get in this case also some vacuum induced non-linearities.

We will not enter here into details of the quantum theory of gravitation and may remark only that it predicts the possibility of mutual transmutations of gravitons, as quanta of gravitational waves, into habitual matter i.e. in electrons-positrons and photons and vice-versa; the validity of the equivalence of inertial and gravitational masses is limited by quantum corrections [1]. One may hope that these conclusions reached for the weak field approxim-

ation will retain their essential validity in the general case. Indeed quite apart from any quantum theory of the vacuum it would be interesting to prove (or disprove) the existence of gravitational waves and to see whether their energy is capable of acquiring the form of habitual matter. If our hypothesis of gravitational transmutations proves to be correct these latter reactions must be taken into account in cosmological considerations.

The basic relations of the theory run as follows.

Taking for the sake of simplicity the case of scalar (pseudoscalar) particles interacting with gravitation one can put the Lagrangian into the form

$$\mathcal{L} = \frac{1}{4} \{ \varphi(x), S\varphi(x) \} \quad (\{...\} \text{ mean anticommutator})$$

where

$$S\varphi = g^{\alpha\beta} \frac{\partial^2 \varphi}{\partial x_\alpha \partial x_\beta} + \frac{1}{\sqrt{-g}} \frac{\partial \sqrt{-g}}{\partial x^\alpha} g^{\alpha\beta} \frac{\partial \varphi}{\partial x^\beta} - m^2 \varphi,$$

and the one particle Greenian $G(x, x') = \langle P(\varphi(x)\varphi(x')) \rangle_{\text{vac}}$ satisfies

$$SG(x, x') = \frac{1}{\sqrt{-g}} \delta(x - x'),$$

so that the vacuum value of \mathcal{L} is

$$\mathcal{L}_0 = \frac{1}{2} SG(x, x') \Big|_{x \rightarrow x'}$$

and for the vacuum value of the action function one gets

$$W_{\text{vac}} = -\frac{1}{2} \text{Spur} \ln G + \text{const.}$$

This result is valid also for spinor fields with corresponding extension of spur also for the summation over spinor indices.

If there are no real pairs produced in vacuum by the gravitational field then

$$W_0 = \frac{1}{2} \frac{1}{(2\pi)^2} \int_0^\infty \tau^{-1} d\tau \int \exp[-ikx] \exp[i\sqrt{-g}] S\tau \exp[ikx] (dx)(dk),$$

(τ -proper time, or 5-th coordinate). Passing to the weak field one gets after some calculations, using the supplementary condition $\partial\sqrt{-g}/\partial x^\alpha = 0$, an expression for W_0 which contains a term proportional to the action function of a free gravitational field (with infinite factors); this can be removed by

renormalizing the co-ordinates and gravitational charge (i.e. mass)

$$m \rightarrow \left(\frac{1}{1 + (\kappa m^2 / 2\pi\hbar c) \frac{1}{6} \int_0^\infty \bar{s}^{-2} \exp[-s] ds} \right)^{\frac{1}{2}} m.$$

The second also infinite term in the W_{vac} contains a Dalembertian operator; its removal, or renormalization would be possible only if the initial Lagrangian of the gravitational field possessed a corresponding term with higher derivatives (which is not the case in the habitual Einstein theory).

This expression for W_{vac} permits to consider various effects connected with the polarization of vacuum by the gravitational field, e.g. the probability of the production of pairs of particles by a gravitational field. The higher terms in the expansion of W_{vac} lead with necessity to non-linear additions [1].

We pass now to the pseudoscalar equations of the mesonic field where one can get non-linear supplementary terms either computing with KURDGELADZE the scattering of mesons on mesons through nucleons (Euler's method of calculating electro-magnetic non-linearities computing scattering of light on light via electrons-positrons) or applying eg. the general method of Schwinger, proved to be successful in electromagnetic and scalar cases. We get with MIRIANAŠVILI for the vacuum density of the Lagrangian:

$$\mathcal{L}' = -\frac{1}{2}(2\pi)^{-2}(m^2 + g^2\tilde{\varphi}^2)^{\frac{1}{2}} \exp[-\frac{1}{2}(m^2 + g^2\tilde{\varphi}^2)S_0] W_{-\frac{3}{2}, -1}[(m^2 + g^2\tilde{\varphi}^2)S_0],$$

where W_- is Whittaker's function. For the weak field one gets the previous results of MALENKA and KURDGELADZE

$$\mathcal{L}' = -\frac{m^2}{8\pi^2\hbar c} \left[\frac{1}{-m^2 S_0} + \ln \frac{1}{\gamma m^2 S_0} + 1 \right] \tilde{\varphi}^2 - \frac{1}{(4\pi)^2 (\hbar c)^3} \left[\ln \frac{1}{\gamma m^2 S_0} \right] \tilde{\varphi}^4.$$

The 1-st term goes for the renormalization of mesonic mass, but the second just yields the non-linear addition to the Klein-Gordon equation [2]

$$\square \tilde{\varphi} - \mu^2 \tilde{\varphi} - \frac{g^4}{(\hbar c)^3} \lambda \tilde{\varphi}^3 = 0, \quad (S_0 = \text{cut off value}).$$

$$\lambda = (2\pi)^2 \ln \frac{1}{\gamma m^2 S_0}.$$

We may note that the general structure of the non-linear coefficient can be obtained very simply by determining the source of the meson field by the Thomas-Fermi statistical model.

Quite in the same manner we can obtain vacuum-induced non-linearities in the case of spinor Dirac equations. Taking the interaction Lagrangian of two spinor fields in the form

$$\mathcal{L}' = -g_F(\bar{\chi}\gamma'_5\chi)(\bar{\psi}\gamma_5\psi),$$

where g_F is the interaction constant of the type of the Fermi constant from the theory of β -decay, and admitting that ψ is a given field and χ corresponds to the vacuum state, we get applying Schwinger's formalism

$$(-i\gamma_5\partial_\mu + \mu)\psi(x) = g\gamma_5\psi(x)\langle\chi\gamma'_5\bar{\chi}\rangle_{\text{vac}} = \langle J(x)\rangle_{\text{vac}}.$$

Then one can get the supplementing term to the Lagrangian

$$\mathcal{L}' = \frac{1}{2}(2\pi)^{-2} \int_0^\infty S^{-3} \exp[-i(m^2 + g^2(\bar{\psi}\gamma_5\psi)^2)S] dS,$$

and the vacuum value of the spinor current

$$\langle j(x)\rangle_{\text{vac}} = \frac{\delta\mathcal{L}'}{\delta\bar{\psi}} = -\lambda\bar{\psi}(x)\gamma_5\psi(x)\gamma_5\psi(x),$$

where

$$\lambda = \frac{m^2}{4\pi^3} \frac{g^2}{\hbar c} \left[-\frac{1}{m^2 S_0} + \ln \frac{1}{\gamma m^2 S_0} + 1 \right].$$

So we obtain for the non-linear generalization of the Dirac equation [3]

$$(-i\gamma_5\partial_\mu + m)\psi - \lambda(\bar{\psi}\psi)\psi = 0.$$

Putting $\sqrt{S_0} \sim 10^{-14}$ and $g \approx g_F$ according to the idea of universal Fermi interaction between arbitrary pairs of fermions, one gets for λ a value not far from g_F , though smaller than it. If one introduces the non-linear term in the Dirac equation as a genuine non-linearity (class A), then the value of λ as of any other interaction or self-interaction constant must be taken provisionally in the present day theory from experiment.

Originally we have supplemented Dirac's equation with the non-linear term just of the same type on the ground of general considerations; later Heisenberg pointed out interesting arguments towards omitting the mass term in this non-linear generalized equation [3].

The situation reminds us of the presence of original «mechanical» and vacuum-induced field masses, or of original bare and vacuum-induced charges.

The difference lies here in the cases of pseudo-scalar and spinor non-linearities in the fact that there are no original non-linear constants entering as factors in the vacuum induced terms, which seems to be essential for renormalization.

Without entering into details we remark that like the non-linear equations of mesodynamics which can be exactly solved by means of elliptic functions, non-linearly generalized spinor equations also possess solutions of the wave-type.

From the non-linear spinor equation one can go to the corresponding non-linear equation of the 2-nd order, generalizing the Klein-Gordon equation. One can also in generalizing de Broglie's fusion method apply a somewhat more general version of fusion to non-linear spinor equations with the purpose to get from them the equations of fused particles (SOKOLIK).

We consider the non-linear generalization of spinor Dirac equations to be of great importance. Further developments will show the part played by gradients-containing non-linearities and lead to more precise determination of the non-linear constant of self-interaction λ . This may prove to be of primary importance as it seems natural to lay down just the spinor-non-linear equation as a foundation of some most «natural» contemporary attempt at an unified theory. The primordial field must be homogeneous but must interact with itself, so it will be described by non-linear equations. From this viewpoint λ will be connected with an universal minimal length.

The importance of non-linear spinor equations is stressed also from another point of view by L. DE BROGLIE and J. P. VIGIER who try to construct in this manner a more satisfactory particle model [4].

Leaving these important general questions we concentrate now on a special point connected with a possible determination of a minimal length as a cut-off in the problem of calculating the mass differences of charged and neutral elementary particles, which are due both to electric and magnetic terms. It is tempting to consider the mass differences of baryons as due to the π -field, as they are of the order $\approx g^2/e^2$

The previous calculations of Feynman contained two separate cut off parameters for nucleons and π -mesons, which clearly deprived them of immediate physical sense. We have tried to get at least qualitatively satisfactory results using only a single cut-off parameter. Putting for the operators of mesonic mass

$$m^2 = m_0^2 - ie^2 \int_{-is_0}^{\infty - is_0} dS \int \frac{d^4k}{(2\pi)^4} \exp[-ik^2] \cdot$$

$$\cdot \left\{ \int_{-is_0}^{\infty - is_0} dS ((2\pi_\mu - k_\mu) \exp[-is(m^2 + (\pi_\mu - k_\mu)^2])(2\pi_\mu - k_\mu)) + 4i \right\}.$$

and nucleonic mass, where a magnetic moment of Pauli-type is present

$$M = M_0 + ie^2 \int_{-iS_0}^{\infty - iS_0} dS \int_{-iS_0}^{\infty - iS_0} dt \int \frac{d^4 k}{(2\pi)^4} \exp[-itk^2] \left\{ \left[\gamma_\mu + \frac{\mu}{4M} k_\alpha (\gamma_\mu \gamma'_\alpha - \gamma'_\alpha \gamma_\mu) \right] \cdot \right. \\ \left. \cdot [M - \gamma(\pi - k)] \exp[-is(M^2 - (\gamma(\pi - k))^2)] \left[\gamma_\mu - \frac{\mu}{4M} k_\beta (\gamma'_\mu \gamma'_\beta - \gamma'_\beta \gamma_\mu) \right] \right\}.$$

we get for the difference of masses of mesons and nucleons

$$\Delta m = \frac{\Delta m^2}{2m} = m \frac{e^2 \pi^2}{2(2\pi)^4} \left\{ \int_0^1 dv \exp[-m^2 S_0 / v(v+1)] \left[4 \frac{2v+1}{(1+v)^2 v} + \frac{1}{(1+v)^2 m^2 S_0} \right] + \right. \\ \left. + \frac{1}{m^2 S_0} (5 - 4 \exp[-m^2 S_0 / 2]) - \frac{1}{2} \frac{1}{(m^2 S_0)^2} (1 - \exp[-m^2 S_0 / 2]) \right\}.$$

$$\Delta M = M \frac{e^2 \pi^2}{(2\pi)^4} \frac{1}{S_0 M^2} \left\{ \int_0^1 dv \exp[-S_0 M^2 / v(v+1)] \cdot \right. \\ \cdot \left[2S_0 M^2 \frac{2v+1}{v(v+1)^2} - \frac{1}{(v+1)^2} - 3\mu \left(\frac{1}{1+v} \right)^2 + \mu^2 \left(\frac{1}{S_0 M^2} \frac{v(1+0.5)v}{(1+v)^2} - \frac{3}{4} \frac{1}{(1+v)^3} \right) \right] + \right. \\ \left. + \left(2 + \frac{1}{S_0 M^2} - \frac{\mu^2}{2(S_0 M^2)^2} \right) (1 - \exp[-S_0 M^2 / 2]) \right\} = a + \mu b + \mu^2 c.$$

Taking the cut off value $\sqrt{S_0} = 1.35(\hbar/Mc)$ which leads to a correct mass difference of $(\pi^\pm - \pi^0)$ mesons, one gets for the mass difference of nucleons the right order of magnitude: $\Delta M = 1.3m$ (electronic masses) [5]. But if one chooses $\sqrt{S_0}$ from ΔM , then for Δm one gets too great a value $\sim 40m$. Nevertheless we are inclined to consider these results as significant, as one sees from the calculations, or best of all from corresponding graphs, that even a small variation of the cut-off parameter leads to inadmissible results.

In general it may be felt as very significant that quite different approaches lead to the values of cut-off parameters or of dimensions of particles which lie in fairly narrow limits. Without entering into a detailed analysis of this important question one may remark that many of the cut-off values or radii of nucleons now in current use in the literature fall in this region: $\sim 2 \div 3 \cdot 10^{-14}$ cm (Chew's cut-off in the pseudo-vector meson theory which is considered as the most successful value; the proton radius in the old strong coupling theory; the cut-off in our theory of mass-difference of particles; the Sachs-Takeda value of the proton radius in the theory of scattering of mesons on protons [6]).

On the other hand the determination of the proton radius from electron

scattering (HOFSTADTER *et al.*) or its value deduced in more indirect way from the proton-proton scattering, as well as the cut-off of Bethe-de Hoffmann from the theory of interaction of π -mesons with nucleons in s -state, or Jastrow's repulsive wall from the scattering of nucleons; further, the radius of the repulsive wall in Levy's semi-empirical theory of nuclear forces; the repulsive wall in the semi-qualitative theory of nuclear saturation of Kerimov, all lead to greater values of the order $5 : 7 \cdot 10^{-14}$ cm. While the dimension of a nucleon, i.e. of the mesonic cloud around the core is to be explained by current mesodynamics, the analysis of the core itself will not lead to reconsideration of our concepts of space-time on small distances of the kind proposed some time ago by ourselves and discussed by several authors? [8].

REFERENCES

- [1] D. IVANENKO and A. BRODSKY *Dokl. (C. R.) Ac. Sci. USSR*, **92**, 4, 31 (19537); cfr. IVANENKO and SOKOLOV: *Klassische Theorie des Feldes* (Aus dem Russischen übersetzt Berlin, 1955). In a private discussion during the Turin congress, September 1956, Prof. W. PAULI remarked that the weak field approximation may prove to be inapplicable in the case of gravitation; if so, then one may hope that our conclusions at least retain their qualitative value.
- [2] M. MIRIANAŠVILI: *General Theory of Mesons*, Dr. degree thesis (Russian) 1956. D. F. KURDGELAJDZE: *Candidate degree thesis*, 1954, *Vestnik (Reports) of the Moscow University*, **8** (1954); D. IVANENKO and D. F. KURDGELAJDZE: *Dokl. (C. R.) Ac. Sci. USSR*, **94**, 1, 39 (1954); B. MALENKA: *Phys. Rev.*, **85**, 686 (1952).
- [3] D. IVANENKO: *Phys. Zeits. d. Sowjetunion*, **13**, 141 (1938); D. IVANENKO and M. MIRIANAŠVILI: *Dokl. (C. R.) Ac. Sci. USSR*, **106**, 713 (1956); G. A. SOKOLIK: *Žu. Èksper. Teor. Fiz.*, (Russian) **28**, 13 (1955); **1**, 9 (1955).
- [4] W. HEISENBERG: *Physica*, **19**, 892 (1953); *Zeits. f. Naturfor.*, **5a**, 251, 367 (1950); L. DE BROGLIE: *Une tentative d'interpretation etc.* (Paris, 1956); J. P. VIGIER: *Structure des micro-objets* (Paris, 1956).
- [5] A. BRODSKY, D. IVANENKO and N. KORST: *Dokl. (C. R.) Ac. Sci. USSR*, **105**, 6, 1192 (1955); R. P. FEYNMAN and S. SPEISMAN: *Phys. Rev.*, **94**, 500 (1954); D. PETERMAN: *Helv. Phys. Acta*, **26**, 441 (1954). A somewhat similar view is expressed in the report of Prof. W. HEITLER published in this issue.
- [6] H. A. BETHE and F. DE HOFFMAN: *Mesons and Fields*, **2** (1955); K. A. BRUECKNER: *Reports on the Moscow High Energy Conference* (May 1956), and on the theoretical seminar of the Moscow University (May 1956).
- [7] H. A. BETHE and F. DE HOFFMAN: *Mesons and Fields*, **2** (1955); D. IVANENKO and B. KERIMOV: *Žu. Èksper. Teor. Fiz.*, (Russian), **31**, 105 (1956).
- [8] V. AMBARZUMJAN and D. IVANENKO: *Zeits. f. Phys.*, **64**, 563 (1930); H. S. SNYDER: *Phys. Rev.*, **71**, 38 (1947); P. CALDIROLA: *Nuovo Cimento*, **10**, 1747 (1953); *Pubblicazioni della Sezione di Milano dell'Istituto Nazionale di Fisica Nucleare*, **8** (1956).

Quantum Kinematics and Geometry.

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1. - Introduction.

The passage from the classical to the quantum mechanics is characterized by the introduction of the Planck constant, which allows to measure linear momenta in units cm^{-1} . In the relativistic quantum mechanics we have also the constant c so that all the physical quantities can be measured by powers of a length, by taking $\hbar = 1$ and $c = 1$. *This remarkable circumstance indicates the existence of a deep unity between physics and geometry, non equivalent to that of the general theory of relativity, since \hbar is involved. The wave-particle duality leads essentially to the identification of the momentum to a geometric covariant vector, the dimension of the components of such a vector being precisely that of the inverse of a length.*

The above dimensional considerations led us to examine the relations between the quantum kinematics and the geometry of the space and the space-time. It is necessary to start from the affine geometry, in order to distinguish clearly the contravariant and covariant vectors. *We needed two kinds of affine vector calculus: one for spin-like discrete variables, another for the continuous position and momentum variables.* GRASSMANN [1] developed two kinds of vector calculus: one with an anticommutative product of contravariant vectors, another with a commutative product. The GRASSMANN calculi were not entirely adequate for our research, we had to extend them by the introduction of symbols for both the contravariant vectors V and covariant vectors U . In our paper [2] «On the Clifford and Grassmann algebras I», we discussed a n -dimensional associative vector algebra G_n , in which the symbols (V) and (U) satisfy the anticommutation rules

$$(1) \quad \begin{cases} [(V), (V')]_+ = 0, & [(U), (U')]_+ = 0, \\ [(V), (U)]_+ = \langle V, U \rangle 1_{G_n}, & \langle V, U \rangle = V^i U_i, \end{cases}$$

1_{G_n} denoting the unity of G_n . G_n is an extension of the anticommutative Grassmann algebra and also of the ordinary vector calculus. In reference (2) we introduced also an associative algebra L_n , in which the symbol $\{V\}$ and $\{U\}$ satisfy the following commutation rules

$$(2) \quad [\{V\}, \{V'\}] = 0, \quad [\{U\}, \{U'\}] = 0, \quad [\{V\}, \{U\}] = \langle V, U \rangle 1_{L_n};$$

1_{L_n} denoting the unity of L_n . L_n is an extension of the Grassman commutative algebra. The direct product $G_n \times L_n$ is related to an extension of the ordinary vector analysis.

We shall denote by I_j 's the basic contravariant vectors and by P_j 's the basic covariant vectors: $V = V^j I_j$, $U = U_j P_j$. We have the following commutation rules

$$(3) \quad [(I_j), (I_k)]_+ = 0, \quad [(P_j), (P_k)]_+ = 0, \quad [(I_j), (P_k)]_+ = \delta_j^k 1_{G_n},$$

$$(4) \quad [\{I_j\}, \{I_k\}] = 0, \quad [\{P_j\}, \{P_k\}] = 0, \quad [\{I_j\}, \{P_k\}] = \delta_j^k 1_{L_n}.$$

Equations (3) show that G_n is the Clifford algebra of a $2n$ -dimensional pseudo-euclidean space S_{2n} with the metric quadratic form $\frac{1}{2} X^j Y_j$, the X 's and Y 's denoting the $2n$ cartesian co-ordinates of a generic point of S_{2n} . Since $4a X^j Y_j = \sum (X^j + a Y_j)^2 - \sum (X^j - a Y_j)^2$, the canonical form of the metric quadratic form of S_{2n} contains n positive and n negative squares. G_n over the complex numbers is the Clifford algebra of a $2n$ -euclidean space. G_n is therefore of the order 2^{2n} . L_n is an infinite algebra associated to the symplectic geometry of S_{2n} , as we showed in reference [2].

The metric geometry is a part of the affine geometry. The introduction of the metric g_{jk} distinguishes sub-algebras of G_n : the Clifford algebras associated to the metrics g_{jk} and $-g_{jk}$. Indeed the $\gamma_j^{(+)}$'s and $\gamma_j^{(-)}$'s

$$(5) \quad \gamma_j^{(\pm)} = (I_j) \pm g_{jk} (P_k), \quad [\gamma_j^{(\pm)}, \gamma_k^{(\pm)}]_+ = \pm 2g_{jk} 1_{G_n}, \quad [\gamma_j^{(+)}, \gamma_k^{(-)}]_+ = 0$$

generate two Clifford algebras. The theory of the spinors of the n -dimensional spaces is included in the theory of G_n . Let us introduce the elements q^j and d_j of L_n

$$(6) \quad \sqrt{2} q^j = \{P_j\} + g^{jk} \{I_k\}, \quad \sqrt{2} d_j = \{I_j\} - g_{jk} \{P_k\}.$$

Since

$$(7) \quad [q^j, q^k] = 0, \quad [d_j, d_k] = 0, \quad [d_j, q^k] = \delta_j^k 1_{L_n},$$

the commutation rules of the q 's and d 's are similar to those of the multipliers x^j and the derivatives D_j . L_n is closely related to the differential calculus and

to the Heisenberg quasi-algebra of the position and momentum operators: we can identify the λq 's with the operators for the cartesian co-ordinates and the $-i\hbar\lambda^{-1}d_j$'s with the operators for the components of the linear momentum of a particle in the case of L_3 , λ being a numerical constant with the dimension of a length. We shall take both λ and \hbar equal to 1. The introduction of a fundamental length λ allows a geometrization of the quantum kinematics.

Let us take $g_{jk} = \varepsilon_j \delta_{j,k}$ in equations (5), with $\varepsilon_j = \pm 1$. The element $\alpha \pm \gamma_1^{(+)} \dots \gamma_n^{(+)} \gamma_1^{(-)} \dots \gamma_n^{(-)}$ anticommutes with all the $\gamma^{(\pm)}$'s and $\alpha^2 = 1_{G_n}$. The elements $\alpha \gamma_j^{(\pm)}$ generate a Clifford algebra C'_n corresponding to the metric g_{jk} . All the elements of the algebra generated by the $\gamma^{(\pm)}$'s are commutable with those of C'_n . When n is even, the $\gamma_j^{(\pm)}$'s and $\alpha \gamma_j^{(\pm)}$'s are a set of generators of G_n , which is the direct product of two Clifford algebras corresponding to the same metric. The consideration of the affine geometry of the space-time gives us two commutable algebras of Dirac γ -matrices, which may be associated with two different kinds of particles of spin $\frac{1}{2}$. G_4 contains as sub-algebras the Duffin-Kemmer-Petiau algebras for the particles with spin 0 and 1, as will be shown in Sect. 2. The algebra G_n is a straightforward extension of the vector calculus of the affine geometry of the n -dimensional space. Thus we see that the algebra for the spins 0, $\frac{1}{2}$ and 1 is the complete form of the ordinary affine vector calculus of the space-time.

The linear space of the contravariant vectors of S_{2n} is the direct sum of the linear spaces of the contravariant and covariant vectors of the associate n -dimensional affine space. S_6 is therefore analogous to the phase-space of a particle. By taking $\hbar = 1$, the dimension of a geometric covariant vector becomes the same as that of linear momentum; thereby we may identify S_6 with the phase-space of a particle. In a similar way we can identify S_8 with a kind of relativistic phase-space including different rest-masses. G_n is a Clifford algebra of S_{2n} ; L_n is an algebra of the symplectic group of S_{2n} , as we showed in reference [2]. The theory of G_4 and L_4 leads to the introduction of two new groups in the quantum mechanics: the group of the linear transformations of the 8 variables X^j, Y_j which leave invariant the symmetric bilinear form $X^j Y_j + X^j Y_j$ (28 parameters); the group of the linear transformations which leave invariant the skew bilinear form $X^j Y_j - X^j Y_j$, the symplectic group of S_8 (36 parameters). These linear transformations must involve a length, because of the different dimensions of the X 's and Y 's. It is interesting to notice that the reduction of the indefinite metric quadratic form $X^j Y_j$ of S_8 to the ordinary canonical form $(4a)^{-1} \sum_j \{(X^j + a Y_j)^2 - (X^j - a Y_j)^2\}$ requires the introduction of a constant a with the dimension of the square of a length.

The introduction of the indefinite metric $X^j Y_j$ in S_{2n} does not depend on any choice of the n -dimensional metric. Equations (5) show that G_n is the Clifford algebra of a $2n$ -dimensional space corresponding to the metric $g_{jk}x^j x^k - g^{jk}y_j y_k$, whose canonical form has also n positive and n negative

squares. We can identify these x 's with components of contravariant vectors of the n -dimensional space and the y 's with components of covariant vectors, the x 's and y 's having the same dimension. In order to identify the y 's with components of geometric covariant vectors, it is necessary to introduce again a constant multiplicative factor with the dimension of the square of a length.

2. - The spin algebra G_n .

The general form of the elements I of G_n is

$$(1) \quad I = \sum_{p,q}^{0,\dots,n} (p! q!)^{-1} C_{j_1,\dots,j_p}^{k_1,\dots,k_q} (I^{j_1}) \dots (I^{j_p}) (I_{k_q}) \dots (I_{k_1}),$$

the C 's being numerical coefficients antisymmetric with respect to the j 's and k 's separately. The C 's transform as the components of tensors with the same indices for a change of the basic vectors I_j . G_n is a geometric calculus for the affine objects of the n -dimensional space described by sets of antisymmetric tensors $C_{j_1,\dots,j_p}^{k_1,\dots,k_q}$.

The commutable idempotent elements $(N_j) \equiv (I^j)(I_j)$ and $(\bar{N}_j) \equiv (I_j)(I^j)$ play a central role in the theory of G_n . Let us introduce the elements $(P_{j_1,\dots,j_p}^{k_1,\dots,k_q})$

$$(2) \quad (P_{j_1,\dots,j_p}^{k_1,\dots,k_q}) = (I^{k_1}) \dots (I^{k_q})(P)(I_{j_p}) \dots (I_{j_1}), \quad (P) = (\bar{N}_1) \dots (\bar{N}_n).$$

It is easily seen that $(I_j)(P) = (P)(I^j) = 0$ and

$$(3) \quad (P_{j_1,\dots,j_p}^{k_1,\dots,k_q})(P_{h_1,\dots,h_r}^{i_1,\dots,i_r}) = \delta_{p,r} \delta_{j_1,\dots,j_p}^{i_1,\dots,i_p} (P_{h_1,\dots,h_r}^{k_1,\dots,k_q}).$$

It follows from (3) that the 2^{2n} elements $(P_{j_1,\dots,j_p}^{k_1,\dots,k_q})$ with $p, q = 0, \dots, n$ and $j_1 < \dots < j_p$, $k_1 < \dots < k_q$ are linearly independent. Any I can be expressed as a linear combination of those 2^{2n} elements

$$(4) \quad I = \sum_{p,q} (p! q!)^{-1} A_{k_1,\dots,k_q}^{j_1,\dots,j_p} (P_{j_1,\dots,j_p}^{k_1,\dots,k_q}).$$

By taking the A 's antisymmetrical with respect the j 's and k 's, separately, they transform as components of tensors with the same indices for any change of the I_j 's. Equation (4) shows that G_n is a total matrix algebra. The left-multiplication of any element (Ψ) of $G_n(P)$ by a I is another (Ψ) . G_n is therefore equivalent to the algebra of the linear transformation of the (Ψ) 's. The (Ψ) 's may be considered as the contravariant spinors of the $2n$ -dimensional pseudo-euclidean space S_{2n} having G_n as its Clifford algebra; the covariant spinors of S_{2n} are the elements of the linear space $(P)G_n$.

The invariant idempotent orthogonal elements $(\Pi_p) = (p!)^{-1} \sum_j (P_{j_1 \dots j_p}^{j_1 \dots j_p})$ are important, because $(\Pi_p)G_n(P)$ is equivalent to the linear space of the covariant antisymmetric tensors $A_{j_1 \dots j_p}$ of the n -dimensional affine space.

We have $\sum_p^{0, \dots, n} (\Pi_p) = 1_{G_n}$, therefore the spinor (Ψ) of S_{2n} is the sum of the elements $(\Pi_p)(\Psi)$ corresponding to antisymmetric covariant tensors of our affine space. Thus we see how the spinors of a $2n$ -dimensional space are built with covariant antisymmetric tensors of a n -dimensional affine space.

G_n over the complex numbers is the n -dimensional analogue of the Jordan-Wigner algebra of the emission and absorption operators of the second quantization for fermions. (P) corresponds to the projector of the vacuum, when (I_j) is assimilated to an absorption operator and (I) to an emission operator. (Ψ) corresponds to a state-vector of the fermion field. The (N_j) 's correspond to the occupation-number operators. The operator for the total number of particles corresponds to the element $(N) = \sum (N_j)$ associated to the tensor δ_j^k by the equation (1).

The two kinds of contravariant half-spinors of S_{2n} are the elements $(\Pi_{\pm})(\Psi)$, (Π_+) denoting the sum of the (Π_p) 's corresponding to even values of p and (Π_-) the sum of those corresponding to odd p 's. The element $(\omega) = (\Pi_+) - (\Pi_-)$ plays an important rôle. Since $(\Pi_p)(I_j) = (I_j)(\Pi_{p+1})$ and $(I)(\Pi_p) = (\Pi_{p+1})(I)$, $(\omega)(I)(\omega) = -(I): I' \rightarrow (\omega)I(\omega)$ is the automorphism of G_n induced by the reflection $V \rightarrow -V$ of the n -dimensional affine space. The two kinds of covariant half-spinors of S_{2n} are the elements of the linear space $(P)G_n(\Pi_+)$ and $(P)G_n(\Pi_-)$.

The elements $(I)(\Pi_p)$, $(\Pi_p)(I_j)$ and $(\Pi_p) + (\Pi_{p+1})$ generate a sub-algebra $D_{n,p}$. We shall write $(\Pi_{-1}) = (\Pi_{n+1}) = 0$, in order to extend the definition of D_n to $p = -1$ and $p = n$. When n is even, all the $D_{n,p}$'s are irreducible Duffin-Kemmer-Petiau algebras; all the irreducible Duffin-Kemmer-Petiau algebras can be obtained in this way, when n is even. The β -generators of $D_{n,p}$ are

$$(5) \quad \beta_j^{(p)} = (\Pi_p)(I_j) + g_{jk}(I^k)(\Pi_p), \quad \beta_j^{(p)}\beta_h^{(p)}\beta_k^{(p)} + \beta_k^{(p)}\beta_h^{(p)}\beta_j^{(p)} - g_{hj}\beta_k^{(p)} + g_{hk}\beta_j^{(p)},$$

when $p \neq (n-1)/2$. In the case of $n = 4$, $D_{4,0}$ and $D_{4,3}$ correspond to scalar and pseudo-scalar particles, respectively; $D_{4,2}$ and $D_{4,1}$ correspond to pseudo-vector and vector particles, respectively; $D_{4,-1}$ and $D_{4,4}$ are « trivial » algebras, with nil β -generators. The algebras $D_{n,p}$ and $D_{n,n-p-1}$ are anti-isomorphic. When n is even, all the irreducible Duffin-Kemmer-Petiau algebras are affine, although their β -generators be dependent on the metric g_{jk} .

G_n possesses an important involution $I' \rightarrow \bar{I}'$, the coefficients \bar{A} in the expansion (4) of \bar{I}' being the dual tensors of the A 's

$$(6) \quad \bar{A}_{j_1 \dots j_p}^{k_1 \dots k_p} = (-1)^{(p-q)(p+q-1)/2} \{ (n-p)! (n-q)! \}^{-1} \epsilon_{j_1 \dots j_p}^{k_1 \dots k_n} A_{k_{q+1} \dots k_n}^{j_{p+1} \dots j_n}.$$

This involution transforms (N_i) into $1_{G_n} (N_i)$; it corresponds to the charge-conjugation of the second quantization for fermions.

All the above results are valid for G_n taken over the real numbers or the complex numbers. The possibility of using only real numbers is rather interesting, because the second quantization formalism of Jordan-Wigner seems to depend essentially on the use of complex numbers. It follows from (4) that the A 's are the matrix elements of I considered as a linear operator on the (Ψ) 's, because the $(P^{j_1 \dots j_p})$'s with $j_1 < \dots < j_p$, $p = 0, \dots, n$ are a basis for the (Ψ) 's and $I(P^{j_1 \dots j_p}) = \sum_q (q!)^{-1} A_{k_1 \dots k_q}^{j_1 \dots j_p} (P^{k_1 \dots k_q})$. The matrices of the (I) 's are not hermitian, that of (\bar{I}) being the adjoint of the matrix of (I) . This corresponds to the property of the absorption operators to be the adjoints of the corresponding emission operators. When $g_{jk} = \varepsilon_j \delta_{j,k}$, the $\gamma_j^{(\pm)}$'s corresponding to positive ε_j 's have hermitian matrices, those corresponding to negative ε_j 's have anti-hermitian matrices.

The central-affine transformation $\underline{x}^j = T_k^j x^k$ induces in G_n the automorphism $I \rightarrow \underline{I} = \exp[-(\tau)] I \exp[(\tau)]$, with $(\tau) = \tau_j^k(I)(I_k)$, the linear operator τ being such that $T = e^\tau$. The above rule of associating an element (τ) to a linear operator τ of the n -dimensional space corresponds to the well-known rule of association of a second quantization operator to an operator of the Hilbert space of the first quantization. It follows from the above rule of transformation of the I 's that $(\underline{\Psi}) = \exp[-(\tau)](\Psi)$.

The results of this section can be extended to the case of $n = \infty$, by using a separable Hilbert-space, instead of the finite-dimensional affine space. The Hilbert space is not strictly sufficient, it is necessary to embed it in a convenient linear space. Thus we see that the second quantization with anticommutation rules is essentially a geometric procedure corresponding to a full development of the vector calculus of the separable Hilbert spaces based on the anticommutative product of vectors. The second quantization appears as a completion of the first quantization, which uses only an incomplete vector calculus of the Hilbert space.

It is convenient to formulate in an abstract way the theory of G_n , in order to see better its essential algebraic characteristics. Let Σ_n denote any n -dimensional linear space and Σ'_n its dual. We shall denote the elements of Σ_n by V 's and those of Σ'_n by U 's. The U 's are linear functionals of Σ_n , the value of the functional U for the element V being denoted by $\langle V, U \rangle$. Let the I_j 's denote n linearly independent V 's, which can be taken as a basis of Σ_n . The dual basis of Σ'_n is constituted by the n functionals I^j defined by the conditions $\langle I_j, I^k \rangle = \delta_j^k$. The direct sum of the linear space Σ_n and Σ'_n is a $2n$ -dimensional linear space Σ_{2n} , whose elements W may be taken as sums $V + U$. The linear spaces Σ_n and Σ'_n can be extended into anticommutative Grassmann algebras, by the introduction of anticommutative products $(V_a)(V_b)$ and $(U_a)(U_b)$, whose generators are the (I_j) 's and (I^j) 's, respectively. These two Grassmann algebras

can be embedded into the Clifford algebra G_n of the sum-space Σ_{2n} endowed with the inner product $2(W_a, W_b) = (V_a, U_b) - (V_b, U_a)$, the commutation rule of the (W) 's being $[(W_a), (W_b)] = 2(W_a, W_b)1_{G_n}$. This inner product corresponds to an indefinite metric, whose canonical quadratic form has n positive and n negative squares. *It is interesting to notice that, in the higher form of vector calculus given by G_n , there is a fusion of the two approaches of Grassmann and Hamilton.*

There is a natural symplectic geometry in Σ_{2n} defined by the symplectic product $2(W_a, W_b) = (V_a, U_b) - (V_b, U_a)$. There is a symplectic algebra L_n of Σ_{2n} with the commutation rule $[\{W_a\}, \{W_b\}] = 2(W_a, W_b)1_{L_n}$. In the case of the L_1 of the phase-space S_{2n} , that commutation rule unifies the three commutation rules (1-2). *This approach to L_n shows immediately the relations between the quantum kinematics and the symplectic geometry of the classical phase-space discussed in reference [2].*

The theory of G_4 is clearly related to the well known method of fusion of De Broglie, which allows to derive algebras of particles with spins 0 and 1 by means of two Clifford algebras. Our geometric theory leads naturally to the direct product of two C_4 's and shows clearly the geometric nature of the Duffin-Kemmer-Petiau algebras. We get from equation (5) the interesting formula $\gamma_j^{(\tau)} = \sum_{p=0, \dots, n} \beta_j^{(p)}$, which expresses the generators of a Clifford algebra in terms of those of Duffin-Kemmer-Petiau algebras. This shows in another way how the theory of the spinors can be derived from that of the antisymmetric tensors.

3. - The Heisenberg quasi-algebra \underline{L}_3 .

The general form of the elements A of L_n is

$$(1) \quad A = \sum_{p, q} (p! q!)^{-1} (r_1! \dots r_n!)(s_1! \dots s_n!) C_{j_1 \dots j_p}^{k_1 \dots k_q} \{I^{j_1}\} \dots \{I^{j_p}\} \{I_{k_1}\} \dots \{I_{k_q}\},$$

the C 's being symmetrical with respect to the j 's and k 's, separately; r_a is the number of j 's equal to the integer a and s_a the number of k 's equal to a . *In order to ensure always the existence of the product of I 's, it is necessary to have only a finite number of terms in the right-hand side of equation (1).* It is convenient to drop this restriction; thus we get an algebraic structure \bar{L}_n , which is no more a linear associative algebra, but a quasi-algebra.

Equation (1) shows that L_n is an algebra for the geometric objects described by finite sets of symmetric tensors U , only one for each kind of variance. The sub-algebra generated by 1_{L_n} and the $\{I\}$'s is isomorphic to the ring of polynomials of n variables; the sub-algebra of \bar{L}_n with the same generators is isomorphic to the ring of the formal power series of n variables. It is obvious

that the theory of the affine algebra L_n leads to mathematical analysis. The equivalence of the Heisenberg and Schrödinger pictures of the quantum mechanics results precisely from the fact that the Heisenberg position-momentum quasi-algebra for a system with n degrees of freedom is a kind of algebraic infra-structure of the differential calculus of the functions of n variables. This fundamental fact follows directly from the geometric nature of the Heisenberg quasi-algebra, which is an extension of L_3 .

The Heisenberg quasi-algebra is not equivalent to \bar{L}_3 , but to another quasi-algebra \underline{L}_3 , analogous to the total metric algebra of the (\mathcal{V}) -space discussed in Sect. 2. \underline{L}_n is the quasi-algebra of the \underline{A} 's

$$(2) \quad \underline{A} = \sum_{p,q}^{0,\dots,\infty} (p!q!)^{-1} (r_1! \dots r_n! s_1! \dots s_n!) A_{k_1 \dots k_q}^{j_1 \dots j_p} \{P_{j_1 \dots j_p}^{k_1 \dots k_q}\}.$$

The j 's and k 's run from 1 to n . The r 's and s 's have the same meaning as in (1). The A 's are numerical coefficients symmetrical with respect to the j 's and k 's, separately. The elements $\{P_{j_1 \dots j_p}^{k_1 \dots k_q}\}$ are symmetrical with respect to the j 's and k 's, separately, and have the following multiplication rule

$$(3) \quad \{P_{j_1 \dots j_p}^{k_1 \dots k_q}\} \{P_{j'_1 \dots j'_{p'}}^{k'_1 \dots k'_{q'}}\} = \delta_{r_1}^{s'_1} \dots \delta_{r_n}^{s'_n} \{P_{j_1 \dots j_p}^{k_1 \dots k_q}\}.$$

The unity of \underline{L}_n is

$$(4) \quad 1_{\underline{L}_n} = \sum_p^{0,\dots,\infty} \{H_p\}, \quad \{H_p\} = \sum_j (p!)^{-1} (r_1! \dots r_n!) \{P_{j_1 \dots j_p}^{j_1 \dots j_p}\}.$$

The $\{H_p\}$'s are orthogonal idempotent elements of \underline{L}_n . We shall define the $\{I\}$'s as follows

$$(5) \quad \{I_j\} = \sum_p^{0,\dots,\infty} \sum_{j_1 \dots j_p}^{1,\dots,n} (p!)^{-1} (r_1! \dots r_n!) \{P_{j_1 \dots j_p}^{j_1 \dots j_p}\} (r_j + 1)^{\frac{1}{2}},$$

$$(6) \quad \{I^j\} = \sum_p^{0,\dots,\infty} \sum_{j_1 \dots j_p}^{1,\dots,n} (p!)^{-1} (r_1! \dots r_n!) \{P_{j_1 \dots j_p}^{j_1 \dots j_p}\} (r_j + 1)^{\frac{1}{2}},$$

r_a denotes the number indices j_1, \dots, j_p equal to the integer a . It follows from the definitions (5)-(6) that

$$(7) \quad [\{I_j\}, \{I_{k_j}\}] = 0, \quad [\{I^j\}, \{I^k\}] = 0, \quad [\{I^j\}, \{I^k\}] = \delta_j^k 1_{\underline{L}_n},$$

$$(8) \quad \{P_{j_1 \dots j_p}^{k_1 \dots k_q}\} = (r_1! \dots r_n! s_1! \dots s_n!)^{-\frac{1}{2}} \{I^{k_1}\} \dots \{I^{k_q}\} \{I_{j_1}\} \dots \{I_{j_p}\}.$$

Equations (7) show that \underline{L}_n includes an algebra equivalent to L_n . In order to render \underline{L}_n into an affine algebra, it suffices to assume that the elements $\{P_{j_1 \dots j_p}^{k_1 \dots k_q}\}$ depend on the choice of the cartesian co-ordinate system and transform in the same way as components of tensors with the same indices; in

particular $\{P\}$ must have the behaviour of a scalar. The equivalence with the matrix formalism for a system with n degrees of freedom is clearly seen by the introduction of the following notations

$$(9) \quad A_{k_1, \dots, k_q}^{j_1, \dots, j_p} = a_{s_1, \dots, s_n}^{r_1, \dots, r_n}, \quad \{P_{j_1, \dots, j_p}^{k_1, \dots, k_q}\} \quad \{\Psi_{r_1, \dots, r_n}^{s_1, \dots, s_n}\}.$$

Equation (2) becomes

$$(10) \quad \underline{A} = \sum_{r, s}^{0, \dots, \infty} a_{s_1, \dots, s_n}^{r_1, \dots, r_n} \{\psi_{r_1, \dots, r_n}^{s_1, \dots, s_n}\}.$$

The a 's are matrix elements of the \underline{A} 's considered as linear operators of the vector space $\underline{L}_n\{P\}$, the application of \underline{A} to any element $\{\Psi\}$ of this space being simply its left-multiplication by \underline{A} . *It is important to notice that the matrices of $\{I_j\}$ and $\{P\}$ are adjoint.*

\underline{L}_n over the complex numbers is the n -dimensional analogue of the second quantization formalism for bosons, the $\{I_j\}$'s corresponding to the absorption operators and the $\{P\}$'s to the emission operators. $\{P\}$ corresponds to the projector of the state-vector of the boson field describing the vacuum. The elements $\{N_j\} = \{P\}\{I_j\}$ are analogous to the occupation-number operators of the boson field. *Thus we see that the boson second quantization formalism is simply a geometric algebra \underline{L}_∞ of a separable Hilbert space.* It follows from equation (8) that the general form of the $\{\Psi\}$'s is

$$(11) \quad \{\Psi\} = \sum_s a_{s_1, \dots, s_n} \{\psi^{s_1, \dots, s_n}\} = \sum_s \bar{a}_{s_1, \dots, s_n} \{P\}^{s_1} \dots \{I\}^{s_n} \{P\}.$$

The $\{\Psi\}$'s correspond to the wave functionals of the quantized boson field. Equation (11) is the analogue of the Fock expansion of the wave functionals of the boson field. *Each $\{\Psi\}$ is associated to a formal power series $\sum_s \bar{a}_{s_1, \dots, s_n} \cdot (z^1)^{s_1} \dots (z^n)^{s_n}$ of n variables z^j . $\{I_j\}\{\Psi\}$ is associated to the series obtained from that corresponding to $\{\Psi\}$ by the derivation of its terms with respect to z^j .*

The $\{\Psi\}$'s for which $\sum_s |a_{s_1, \dots, s_n}|^2 < \infty$ constitute a Hilbert space H_n . The power series associated to the elements of H_n converge for all the values of the z^j 's and represent integral functions of the z^j 's. We shall now see that H_n is equivalent to the Hilbert space of the states of a system with n degrees of freedom. Let us take $\sqrt{2}q^j = \{P\} \mid \{I_j\}$. It is easily seen that

$$(12) \quad \{\psi^{s_1, \dots, s_n}\} = h_{s_1, \dots, s_n}(q)\{P\}, \quad \{P\} = \pi^{n/4} \exp\left[\frac{1}{2} \sum_j (q^j)^2\right]\{P\}.$$

The h 's are normalized Hermite functions

$$(13) \quad h_{s_1, \dots, s_n}(q) = \pi^{-n/4} \prod_j \{2^{s_j}(s_j!)\}^{-\frac{1}{2}} \exp\left[-\frac{1}{2}(q^j)^2\right] H_{s_j}(q^j).$$

It follows from equation (12) and (11) that

$$(14) \quad \{\Psi\} = \sum_{s_1, \dots, s_n} a_{s_1, \dots, s_n} h_{s_1, \dots, s_n}(q) \{\underline{P}\}.$$

$\{\Psi\}$ is associated to a formal series of Hermite functions of n real variables x^j : $\sum_{s_1, \dots, s_n} a_{s_1, \dots, s_n} h_{s_1, \dots, s_n}(x)$. When $\{\Psi\}$ belongs to H_n its associate Hermite series converges in the mean to a function $F(x)$ of Lebesgue integrable squared absolute value, over the whole x -space.

The $\{\Psi\}$'s not belonging to H_n correspond to functions of non square integrable absolute value and also to distributions. Thus the element $(2\pi)^{-n/2} \sum_{s_1, \dots, s_n} i^{s_1 + \dots + s_n} h_{s_1, \dots, s_n}(u) h_{s_1, \dots, s_n}(q) \{\underline{P}\}$ corresponds to the function $\exp[i \sum_j u^j x^j]$ and $\delta_u - \sum_s h_{s_1, \dots, s_n}(u) h_{s_1, \dots, s_n}(q) \{\underline{P}\}$ to $\prod_j \delta(x^j - u^j)$. The Fourier transformation can be easily extended to all the $\{\Psi\}$'s: the Fourier transform of h_{s_1, \dots, s_n} being $i^{s_1 + \dots + s_n} h_{s_1, \dots, s_n}$, we can take as Fourier transform of $\{\Psi\}$ the element $\sum_{s_1, \dots, s_n} i^{s_1 + \dots + s_n} a_{s_1, \dots, s_n} h_{s_1, \dots, s_n}(q) \{\underline{P}\}$. The derivation can be defined for all the $\{\Psi\}$'s by means of the d_j 's

$$(15) \quad \sqrt{2} d_j = \{\mathbf{I}_j\} - \{\mathbf{I}\}, \quad [d_j, q^k] = \delta_j^k 1_{\underline{L}_n}^{\frac{1}{2}}, \quad d_j \{\underline{P}\} = 0,$$

$d_j \{\Psi\}$ is associated to the formal series obtained from that corresponding to $\{\Psi\}$ by derivation of its terms with respect to x^j . We can obtain a kind of integration by means of the inner product $(\{\Psi^I\}, \{\Psi^{II}\}) = \sum_{s_1, \dots, s_n} a_{s_1, \dots, s_n}^I (a_{s_1, \dots, s_n}^{II})^*$. This integration may have a meaning even when the $\{\Psi\}$'s do not correspond to functions. Thus we have $(\{\Psi\}, \delta_u) = F(u)$, when $\{\Psi\}$ is associated to the function $F(x)$.

The above results show that \underline{L}_n gives a powerful extension of the classical mathematical analysis and of the theory of the Hilbert space. It is noteworthy that most of those results do not depend essentially on the field of real or complex numbers over which \underline{L}_n is taken. In particular, the continuity properties of those fields are irrelevant. We might even replace the fields by more general algebraic structures. It is possible that a further development of the quantal physics will require a deep revision of our intuitive picture of space and time. This does not necessarily mean that the tools of mathematical analysis will need essential modifications, because they seem to depend little on the properties of continuity.

It is clear that the concept of function is not the natural one for the quantal physics: the concept of element of a $\{\Psi\}$ -space is certainly more adequate. From the analytical point of view, this concept is equivalent to that of a linear functional completely determined by its values for the functions h_{s_1, \dots, s_n} . Indeed, the coefficients a_{s_1, \dots, s_n} may be considered as the values of such a functional for those functions. Conversely any such functional gives us a set of

coefficients α_{s_1, \dots, s_n} , as its values for the functions h_{s_1, \dots, s_n} , which determine it completely and allow to define an associate $\{\Psi\}$.

The definition of the q 's and d 's used in this section corresponds to that given by (1-6), with the euclidean metric $g_{jk} = \delta_{j,k}$. *The q 's are hermitian operators of the $\{\Psi\}$ -space; the d 's are anti-hermitian operators.* In the case of a pseudo-euclidean metric $g_{jk} = \varepsilon_j \delta_{j,k}$, the q 's corresponding to negative ε_j 's are anti-hermitian and the d_j 's hermitian. The variable x^j must then be taken as imaginary.

The theory of \underline{L}_n gives a remarkable fusion of the Schrödinger and Heisenberg formalisms, because the wave-functions and the operators for the observables are all associated to elements of the quasi-algebra. Moreover we have also the equivalent of symbolic functions such as Dirac's δ and its derivatives. It is interesting to notice that there is a simple closed expression for the element δ_u associated to the n -dimensional Dirac function

$$(16) \quad \delta_u = (4\pi)^{-n/4} \exp \left[-\frac{1}{2} \sum_j (\bar{d}_j^2 + 2u^j \bar{d}_j) \right] \{P\}.$$

A closed expression for the element associated to the derivative $D_1^{r_1} \dots D_n^{r_n}$ of $\delta(\mathbf{x} - \mathbf{u})$ can be obtained from (16) by left-multiplication of both sides by $\bar{d}_1^{r_1} \dots \bar{d}_n^{r_n}$.

Equation (2) shows that \underline{L}_n is a calculus for the geometric objects described by finite or infinite sets of symmetric tensors $A_{k_1, \dots, k_q}^{j_1, \dots, j_p}$. Another such calculus is given by the quasi-algebra \bar{L}_n . The great advantage of \underline{L}_n is obviously its equivalence with a quasi-algebra of infinite matrices. *It is remarkable that the geometric quasi-algebra of the symmetric tensors \underline{L}_n be automatically a theory of functions, measures and distributions of n real variables.* The modern theory of the functions of real variables showed that the concept of continuous function of n real variables is a special case of the concept of measure of sets, i.e. of the distribution of mass or charge in a n -dimensional space. Not all the distributions of charge can be described by measures, the subtler ones correspond to the Schwarz distributions and perhaps to still more elaborate analytical concepts. *The geometric algebra \underline{L}_n is a generalized theory of measures of the n -dimensional space, non equivalent to the Schwarz distribution theory.*

In the quantum mechanics, \underline{L}_n appears as a tool for the description of probability distributions associated to dynamical systems with n degrees of freedom. These probability distributions describe ultimately non intuitive distributions of matter in space. *The use of probability in the quantum mechanics may be a means to relate the micro-geometric properties of matter at the atomic level wit the macroscopic geometric concepts. It is clear that the ordinary macro-geometric concepts of position etc. are not applicable to matter at the atomic level, which occupies space in very subtle ways described by the geometric algebras. A further clarification of the foundations of the quantum mechanics requires a*

better understanding of the picture of space involved in the geometric algebras.

Our analysis of the symmetric tensors of the n -dimensional affine space led us to the introduction of an infinite dimensional linear space $\underline{L}_n\{P\}$. The distinction of the $\{\Psi\}$'s of the Hilbert space H_n is not affine invariant: H_n is associated to the metric euclidean geometry of the n -dimensional space. The unitary metric of H_n is an extension of the euclidean metric of the n -dimensional space. Indeed, the euclidean metric can be extended to the linear space of the symmetric covariant tensors of order q by taking as the norm of the tensor $A_{k_1 \dots k_q}$ the square root of the sum $\sum_k (q!)^{-1} (s_1! \dots s_n!) |A_{k_1 \dots k_q}|^2$. The square of the norm of a $\{\Psi\}$ is simply the sum of the squares of the norms of its tensors $A_{k_1 \dots k_q}$, $q = 0, \dots, \infty$.

The theory of \underline{L}_n deals essentially with the linear space of the $\{\Psi\}$'s and its linear operators. The analysis of the properties of this linear space can be done with more depth by the introduction of its geometric algebras G and \underline{L} , i.e. of the second quantization formalisms for bosons and fermions. The theory of the quantized fields is therefore associated with a higher stage of the geometric analysis of the space-time. In the case of the n -dimensional space, it is necessary to consider the direct product of G_n and \underline{L}_n , which is a generalization of the vector analysis. In a similar way, in the case of the infinite dimensional $\{\Psi\}$ -space we must take the direct product of the two second quantization quasi-algebras, which is a quasi-algebra for interacting fermion and boson fields. The identification of \underline{L} with the quantum kinematics requires a fundamental length λ , which is also involved in our geometric approach to the quantum field theory.

4. - The harmonic oscillators of \underline{L}_n .

The elements $\{N_j\} = \{\mathbf{I}^j\}\{\mathbf{I}_j\}$ of \underline{L}_n correspond to the occupation-number operators of the boson second quantization. They play a central part in the theory of \underline{L}_n , because $(\{N_j\} - s_j 1_{\underline{L}_n})\{P_{j_1 \dots j_p}^{k_1 \dots k_p}\} = 0$, $\{P_{j_1 \dots j_p}^{k_1 \dots k_p}\}(\{N_j\} - r_j 1_{\underline{L}_n}) = 0$. Since $\{N_j\} = \frac{1}{2}((q^j)^2 - (d_j)^2 - 1_{\underline{L}_n})$, $\{N_j\}$ is analogous to the hamiltonian of a one-dimensional harmonic oscillator. \underline{L}_n is essentially the quantum mechanics of a system of n one-dimensional uncoupled harmonic oscillators.

The $\{N_j\}$'s are a special case of the elements $\{N_v\} = \{\mathbf{V}\}^+ \{\mathbf{V}\}$, \mathbf{V} being a real unit vector $\sum_j V^j = 1$; $\{\mathbf{V}\}^+ = \sum_j V^j \{\mathbf{I}^j\}$ is the adjoint of $\{\mathbf{V}\}$ as an operator of the $\{\Psi\}$ -space. The eigenvalues of $\{N_v\}$ are the non negative integers, because $[\{\mathbf{V}\}, \{\mathbf{V}\}^+] = 1_{\underline{L}_n}$. $\{N_v\}$ does not depend on the sense of \mathbf{V} , it is associated to its direction. The $\{N_j\}$'s correspond to the co-ordinate axes.

The existence of elements with non negative integer eigenvalues associated to the directions of the n -dimensional space is a very remarkable property of \underline{L}_n , still enhanced by the fundamental part played by these elements. It is

important to notice the metric nature of the $\{N_v\}$'s. The definition of a vector of length unity, presupposes a choice of the unit of length. We have the natural unit of length λ , which was identified to 1. Strictly speaking the eigenvalues of the $\{N_v\}$'s are the non negative integral multiples of λ^2 . There is a kind of quantization of the square of the length of a vector. In the case of a Hilbert space, this quantization of the square of the norm gives the integral numbers of bosons in the one-boson states. The $\{N_v\}$'s corresponding to orthogonal $\{V\}$'s are commutable, otherwise not.

There are natural relations between \underline{L}_n and the theory of probability. The eigenvalues of $\{N_v\}^{\frac{1}{2}}$ are the mean square displacements of a particle in a one dimensional random walk of step 1, after integral numbers of steps. It is interesting to notice that the fundamental element $\{P\}$ is associated to the gaussian function $\pi^{-n/4} \exp[-\frac{1}{2} \sum_j x_j^2]$. The true nature of those relations between \underline{L}_n

and the theory of probability is not yet clear. It is well known that the theory of probability is closely related to that of the averages of functions of infinite numbers of variables (see PAUL LÉVY: *Problèmes concrets d'analyse fonctionnelle* (Paris, 1951); especially the third part). The central part played by the gaussian and the Hermite functions in the theory of \underline{L}_n indicates clearly that the stage of the analysis of the n -dimensional space given by the present form of the theory of \underline{L}_n corresponds to some kind of averaging over a linear space of infinite dimensionality. As a matter of fact, such a space appears already in our treatment: the $\{\Psi\}$ -space. The point of co-ordinates x of the n -dimensional space is associated to the element δ_x of the $\{\Psi\}$ -space. \underline{L}_n is a link between the micro-geometry and the macro-geometry of the ordinary objects. The probabilistic results seem to be due to the averaging over the microscopic properties which lead to the familiar geometric properties. This suggests that the micro-geometric properties begin to appear more clearly in physics at the level of the quantum theory of fields.

The linear transformations $I_j \rightarrow e^{a_j} I_j$ correspond to changes of the unit vectors of the co-ordinate axes. They induce in \underline{L}_n a n -parameter abelian group of automorphisms $\underline{A} \rightarrow \exp[-\sum_j a_j \{N_j\}] \underline{A} \exp[\sum_j a_j \{N_j\}]$. In particular we have $\{\Psi\} \rightarrow \exp[-\sum_j a_j \{N_j\}] \{\Psi\}$. The $\{N_j\}$'s are essentially the infinitesimal transformations of that abelian group of automorphisms. By taking imaginary values for the a_j 's, we get the n -dimensional analogue of the change of the phases of the basic vectors in a Hilbert space, well known from the theory of the gauge transformation of the quantum mechanics. The consideration of real values of the a_j 's shows clearly the geometric nature of the group underlying the gauge transformations.

By taking all the a_j 's equal to a , we get the important one parameter group of automorphisms $\underline{A} \rightarrow \exp[-a\{N\}] \underline{A} \exp[a\{N\}]$, with $\{N\} = \sum \{N_j\}$, induced in \underline{L}_n by the similitudes $V \rightarrow e^a V$ of the n -dimensional space. The element $\{N\}$ does not depend on the choice of the I_j 's, because it is the contracted

product V_i, U_i of the symbolic vectors V_i and U_i of components $\{I\}$ and $\{I_j\}$, respectively. $\{N\}$ is the analogue of the element (N) of G_n , being associated to the fundamental tensor δ_j^k and to the operator unity on the V 's. $\{N\}$ corresponds to the operator for the total number of particles of the boson second quantization.

It is easily seen that $\exp[(i\pi/2)\{N\}]\{\Psi\}$ is the Fourier transform of $\{\Psi\}$ defined in Sect. 3. *The imaginary similitude $V \rightarrow -iV$ induces the Fourier transformation in the $\{\Psi\}$ -space; $\{\Psi\} \rightarrow \exp[a\{N\}]\{\Psi\}$ and $\{\Psi\} \rightarrow \exp[\sum a_j\{N_j\}]\{\Psi\}$ are generalizations of the Fourier transformation.* This association of the Fourier transformation to a complex similitude is very remarkable and gives a simple geometric foundation for the theory of the Fourier transformation. The automorphism $\Gamma \rightarrow \exp[(i\pi/2)(N)]\Gamma \exp[(-i\pi/2)(N)]$ of G_n is analogous to the Fourier automorphism of \underline{L}_n ; it transforms the $\gamma_j^{(+)}$'s into the $-i\gamma_j^{(-)}$'s.

$\{N\}$ is the hamiltonian, without zero-point term, of a n -dimensional isotropic harmonic oscillator. The automorphisms of \underline{L}_n corresponding to the unitary transformations $\underline{A} \rightarrow \exp[-it\{N\}]\underline{A} \exp[it\{N\}]$ generated by the motion of the isotropic oscillator are powers of the Fourier transformation of the \underline{A} 's. The inverse Fourier transformation corresponds to $t = \pi/2$ and the spatial reflection to $t = \pi$. *Our geometric theory gives the deep reason of the relations between the spatial reflection and the iterated Fourier transformation.* Those automorphisms correspond to the changes of phase $V \rightarrow e^{iz}V$ of the vectors of the n -dimensional space.

A complete basis for the infinitesimal transformations of the $\{\Psi\}$ -space induced by central-affinities of the n -dimensional space is constituted by the $\{M_{jk}\} = \{I\}\{I_k\} - \{I^k\}\{I_j\} = q^j d_k - q^k d_j$ and the $\{S_{jk}\} = \{I^j\}\{I_k\} + \{I^k\}\{I_j\}$. The $\{M_{jk}\}$'s correspond obviously to the infinitesimal n -dimensional rotations and the $\{S_{jk}\}$'s to the infinitesimal deformations. We have $\{S_{jj}\} = 2\{N_j\}$. Our theory introduces the deformations together with the rotations, whereas ordinarily only the rotations are considered. *We see that the infinitesimal dilatations play a central rôle in the theory of \underline{L}_n .* The analogue of $\{M_{jk}\}$ in G_n is $(M_{jk}) = (I)(I_k) - (I^k)(I_j) = \frac{1}{2}(\gamma_j^{(+)}\gamma_k^{(+)} - \gamma_j^{(-)}\gamma_k^{(-)})$.

The fundamental importance of the isotropic harmonic oscillator associated to the basic length indicates that it must be of significance in physics. It seems satisfactory to assume that the basic length is the Compton wave length of the π -meson. In the shell model of the nucleus, the isotropic harmonic oscillator is of importance. *It seems therefore reasonable to associate the shell model of the nucleus to the isotropic oscillator of \underline{L}_3 .* The spin-orbit coupling cannot be included in the theory of \underline{L}_3 , which does not contain spin-like variables.

The non relativistic theory of the spin $\frac{1}{2}$ particles requires the introduction of the direct product of the Pauli spin algebra by \underline{L}_3 . The Pauli algebra is a sub-algebra of the reducible C_3 . C_3 is of the order 8 and may be generated

by the element $\theta = i\gamma_1\gamma_2\gamma_3$ and the three components of the spin vector σ , $\sigma_k = i\gamma_h\gamma_j$, (h, j, k) denoting a circular permutation of (1, 2, 3). The element of C_3 associated to the euclidean tensor A_{jk} is $\sum A_{jk}\gamma_j\gamma_k$. The spin-orbit element $\sum_{j,k} \{M_{jk}\}\gamma_j\gamma_k$ is therefore associated to the symbolic antisymmetric tensor of components $\{M_{jk}\}$. The element \mathcal{Q} associated to the symbolic tensor $\{I\}\{I_k\}$ is $\mathcal{Q} = \sum \{I\}\{I_k\}\gamma_j\gamma_k = \{N\} + \frac{1}{2} \sum \{M_{jk}\}\gamma_j\gamma_k$. Thus we get quite naturally an isotropic oscillator with an exceedingly strong spin-orbit coupling, by considering the complete symbolic tensor of the infinitesimal central-affine transformations. The involution of G_3 discussed in Sect. 2 induces an involution in $C_3 \times \underline{L}_3$, which transforms \mathcal{Q} into $\overline{\mathcal{Q}} = \{N\} - \frac{1}{2} \sum \{M_{jk}\}\gamma_j\gamma_k$ and changes the sign of the spin-orbit interaction. The above considerations do not give a satisfactory spin-orbit interaction for the shell-model oscillator. It is likely that the nuclear spin-orbit interaction depends essentially on relativistic effects. The above results are nevertheless interesting because they show how naturally the geometric algebras lead to the kinds of forces involved in the shell-model.

5. — Isotopic spin and projective geometry.

An algebra of vectors cannot give a satisfactory affine calculus, because the vectors are non localized objects. The anticommutative Grassmann algebra of vectors is included in the algebra of points, the contravariant vectors being considered as differences of points. This algebra of points can also be applied to the projective geometry, as well known. We shall now develop an algebra, which is an extension of the Grassmann algebra of points. Let the X^μ 's, μ running from 0 to n , denote polyhedric co-ordinates of the points of a n -dimensional space. The projective transformations are given by homogeneous linear transformations of the X 's. The polyhedric co-ordinates of hyperplanes will be denoted by Y_μ 's. We shall introduce two $(n+1)$ -dimensional dual linear spaces whose vectors \mathbf{X} and \mathbf{Y} have the components X^μ and Y_μ , respectively. The G -algebra associated to this pair of dual linear spaces will be denoted by G'_n . G'_n is isomorphic to a G_{n+1} ; it is generated by the elements (\mathcal{J}_μ) . (\mathcal{J}^μ) corresponding to the basic vectors of two dual basis of the above linear spaces. The commutation rules of the (\mathcal{J}) 's are

$$(1) \quad [(\mathcal{J}_\mu), (\mathcal{J}_\nu)]_+ = 0, \quad [(\mathcal{J}^\mu), (\mathcal{J}^\nu)]_+ = 0, \quad [(\mathcal{J}_\mu), (\mathcal{J}^\nu)]_+ = \delta_\mu^\nu 1_{G'_n}.$$

The projectivity $X^\mu \rightarrow T^\mu_\nu X^\nu$ induces in G'_n the inner automorphism $\Gamma' \rightarrow \exp[-(S)]\Gamma'\exp[S]$, Γ' denoting a generic element of G'_n and (S) the element $S^\nu_\mu(\mathcal{J}^\mu)(\mathcal{J}_\nu)$, the matrix S^ν_μ being any determination of the logarithm

of the non-singular matrix T_{μ}^r of the projectivity. The linear transformations of X 's into Y 's correspond to correlations, they do also induce inner automorphisms in G_n' . The affine transformations are a particular case of the projective ones, characterized by leaving invariant the hyperplane at infinity.

For the discussion of the affine transformations, it is convenient to take the X^{μ} 's and Y_{μ} 's as homogeneous cartesian point and hyperplane co-ordinates. Thus X^0 and Y_0 behave as scalars and the X^j 's and Y_j 's as components of contravariant and covariant vectors, respectively, for central-affine transformations. Since $x^j = X^j/X^0$, the translation $x^j \rightarrow x^j + V^j$ corresponds to $X^0 \rightarrow X^0$, $Y_0 \rightarrow Y_0 - Y_j V^j$, $X^j \rightarrow X^j + X^0 V^j$, $Y_j \rightarrow Y_j$. The \mathcal{J}_j 's can be identified with the I_j 's, but the \mathcal{J} 's do not transform in the same way as the I 's for translations. \mathcal{J}_0 corresponds to the origin of the co-ordinates and \mathcal{J}^0 to the hyperplane at infinity. *The sub-algebra of G_n' generated by those (\mathcal{J}_j) 's and (\mathcal{J}^j) 's is isomorphic to G_n , but cannot be identified with G_n when translations are considered, because all the elements of G_n must be invariant for translations of the cartesian frame.*

Let (ω') denote the element of G_n' analogous to the element (ω) of G_n introduced in Sect. 2. (ω') does not depend on the choice of the \mathcal{J} 's and anti-commutes with all the (\mathcal{J}) 's. The elements

$$(2) \quad \tau_+ = (\mathcal{J}^0)(\omega'), \quad \tau_- = (\omega')(\mathcal{J}_0), \quad \tau_3 = 2(\mathcal{J}^0)(\mathcal{J}_0) - 1_{G_n},$$

generate a sub-algebra isomorphic to the Pauli spin algebra, whose elements are commutable with those of the sub-algebra generated by the (\mathcal{J}_j) 's and (\mathcal{J}^j) 's. *G_n' is isomorphic to the direct product of G_n by a Pauli spin algebra. By taking the (\mathcal{J}) 's corresponding to homogeneous cartesian co-ordinates, the elements of the τ sub-algebra are invariant for central-affine transformations leaving fixed the origin of the cartesian co-ordinates.*

The existence of non-localized vectors is characteristic of flat spaces. In a curved space, the vectors are anchored to the points and we must consider the parallel displacement of the vector-body from a point to the neighbouring ones. There is a G_n associated to the flat tangent space at each point, the isomorphic G_n 's at different points being connected by a kind of parallel displacement related to that of the vectors. We have also a G_n' associated to each point and there is no interest in displacing the origin of the co-ordinates from the point of contact in the flat tangent space; the above difficulty of identifying G_n to a sub-algebra of G_n' becomes therefore irrelevant. In the physical case, the flat space-time is an approximation to the real curved space-time.

When only central-affine transformations are considered, the linear space of the homogeneous cartesian Y_{μ} 's is simply the direct sum of the linear spaces of the scalars Y_0 and the covariant vectors of components Y_j . This linear

space is interesting because of its association with the irreducible Duffin-Kemmer-Petiau algebra $D_{n,0}$ of Sect. 2, which is its total metric algebra. In the case of the space-time, $D_{4,0}$ is the Duffin-Kemmer-Petiau algebra of the scalar particles of spin 0; G'_4 is essentially the direct product of G_4 by the G_1 of the one-dimensional linear space of the scalars. We can now identify G_4 with a sub-algebra of G'_4 and the τ sub-algebra with the isotopic spin algebra of the nucleon. G_4 may be considered as the direct product of the Dirac γ -algebras of the electron and the nucleon and G'_4 as the algebra of the discrete variables of the electron and the nucleon.

6. - Alternative approach to the geometric calculus.

The possibility of obtaining the isotopic spin from a G_5 , suggests a new approach to the geometric calculus of the affine spaces. We started from the pair of dual linear spaces of the contravariant and covariant vectors. It is more satisfactory to start from the direct sum of the linear spaces of the contravariant vectors and scalars and its dual, which is the direct sum of the linear space of the covariant vectors and of a second linear space of scalars. The scalars are as fundamental as the vectors, their rôle does not appear clearly, because they are not distinguished from the numbers of the field underlying the linear spaces. The difference between the scalars and the numbers appears in the vector analysis, when scalar functions are considered. The basis in the space of the scalars and contravariant vectors is constituted by the $n+1$ elements I_μ ; the basis in the dual space is constituted by the I^μ 's such that $\langle I_\mu, I^\nu \rangle = \delta_\mu^\nu$. The generators of the G_{n+1} associated to our pair of $(n+1)$ -dimensional dual linear spaces have the commutation rules $[(I_\mu), (I_\nu)]_+ = 0$, $[(I^\mu), (I^\nu)]_+ = 0$, $[(I_\mu), (I^\nu)] = \delta_\mu^\nu 1_{G_{n+1}}$. Thus we get directly an algebra isomorphic to G'_n , which can be identified with the algebra of the discrete variables of the electron and the nucleon, in the case of the space-time. The total metric algebras of our $(n+1)$ -dimensional linear spaces are equivalent to the Duffin-Kemmer-Petiau algebra $D_{n,0}$ and its reciprocal algebra.

The n -dimensional projective group comes in only as the group of the automorphisms of the metric algebra of the $(n+1)$ -dimensional linear space, our $D_{n,0}$. G_{n+1} has a sub-algebra which can be identified to the G_n of our n -dimensional space: the sub-algebra generated by the (I_j) 's and (I^j) 's. We do not have now the difficulty with the translations and G_n presented by G'_n , because the I_j 's and I^j 's are assumed to transform as components of a n -dimensional covariant vector and a n -dimensional contravariant vector, respectively, whereas in the case of G'_n the \mathcal{J}^μ 's and \mathcal{J}_μ 's must transform as the X^μ 's and Y_μ 's, respectively.

We can build a \underline{L}_{n+1} associated to the above pair of dual linear sum-spaces,

which allows to obtain functions and distributions of $n+1$ variables in the case of an n -dimensional case. These functions for the space-time would depend on the space and time variables and also on a fifth scalar variable, whose meaning is not clear. In connection with the new variable there is a new one-dimensional harmonic oscillator hamiltonian.

The direct sum of the linear spaces of the contravariant vectors and the scalars of the three-dimensional space is involved in the theory of the quaternions. Our formalism is not equivalent to the quaternion algebra: it gives a G_4 in the case of a three-dimensional space.

7. - Algebras of the conformal geometry.

We showed in Sect. 1 that G_4 is the direct product of two Clifford algebras equivalent to the Dirac algebra of the γ -matrices. Thus the affine geometry led to the consideration of two basic types of spin $\frac{1}{2}$ fermions. We should expect them to be the lepton (electron-neutrino) and the nucleon (proton-neutron), but this identification requires two new spin-like variables in order to distinguish the electron and neutrino states of the lepton and the neutron and proton states of the nucleon. The passage from G_4 to G'_4 gave us one such variable, which was identified with the isotopic spin of the nucleon. We could get the missing variable by going over from G'_4 to a broader algebra G'_5 , equivalent to a G_6 . We shall now see that there are geometric reasons to introduce a G'_6 .

It is well known that the conformal group of the space-time is important for the particles with zero-mass. This indicates that the algebras of the conformal group may give us the two-valued variable which distinguishes the electron and neutrino states of the lepton. In order to discuss the conformal geometry of an n -dimensional space, it is convenient to embed it in a $(n+1)$ -dimensional space. Let us denote by x^1, \dots, x^{n+1} the cartesian co-ordinates of the $(n+1)$ -dimensional space, chosen in such a way that our n -dimensional space be the hyperplane of equation $x^{n+1} = 0$. The points of this hyperplane can be obtained by stereographic projection from those of the hyperquadric of equation $g_{jk}x^jx^k + (x^{n+1})^2 = 1$, the centre of projection being the point of co-ordinates $x^j = 0, x^{n+1} = 1$. Let the $n+2$ X^0 's be homogeneous co-ordinates: $x^j = X^j/X^0, x^{n+1} = X^{n+1}/X^0$. The X 's of the points of the above hyperquadric will be denoted by ξ 's: $g_{jk}\xi^j\xi^k + (\xi^{n+1})^2 = (\xi^0)^2$. The ξ 's are hyperspherical co-ordinates of the points of the n -dimensional space. It is well known that the conformal transformations of this space are given by linear transformations of its ξ 's leaving invariant the above quadratic equation, when $n > 2$. The Clifford algebra C_{n+2} corresponding to the quadratic form $g_{jk}X^jX^k + (X^{n+1})^2 - (X^0)^2$ is obviously the geometric algebra of the conformal geometry of the n -di-

n -dimensional space with the metric g_{jk} . In the case of the space-time, we get a C_6 , whose spinors have 8 components. We have thus added a new two-valued variable to the spin-like variables involved in the relativistic theory of the electron.

The above G'_{n+2} is a sub-algebra of the G'_{n+1} of the projective geometry of the $(n+1)$ -dimensional space. All the collineations of this space induce inner automorphisms in G'_{n+1} , even if they do not leave invariant the hyperquadric associated to the conformal geometry of the n -dimensional space. The collineations leaving invariant the hyperplane $X^{n+1}=0$ induce in it the projective transformations of our n -dimensional space; those leaving invariant the hyperquadric of equation $g_{jk}X^jX^k+(X^{n+1})^2=(X^0)^2$ correspond to the n -dimensional conformal transformations. We may therefore identify the projective algebra G'_n with the sub-algebra of G'_{n+1} generated by the (\mathcal{J}_μ) , (\mathcal{J}^μ) with $\mu=0, 1, \dots, n$, the (\mathcal{J}_ρ) , (\mathcal{J}^ρ) being the $2(n+2)$ (\mathbf{I}) -generators of G'_{n+1} . The algebra G'_{n+1} is associated to both the projective and conformal geometries of our n -dimensional space. The G'_n of the space-time allows us to include the neutrino in our geometrical picture.

We shall now choose the hyperspherical co-ordinates in a somewhat different way, in order that $x^{n+1}=g_{jk}x^jx^k$, $X^0X^{n+1}=g_{jk}X^jX^k$. The new x^5 of the space-time is a physically interesting variable, because it represents the square of the interval between the origin and the point. The equations of motion of a classical relativistic charged particle can be written as follows [3]

$$\frac{dx^j}{ds} = \frac{\partial K}{\partial p_j}, \quad \frac{dp_j}{ds} = -\frac{\partial K}{\partial x^j}, \quad K = \{g^{jh}(p_j - eA_j)(p_h - eA_h)\}^{\frac{1}{2}},$$

s is the interval along the world-line, treated as a fifth independent variable. K is clearly a constant of the motion, which must be identified with the rest-mass, the formalism allowing the rest-mass to take different values. The rest-mass appears now as a kind of conjugate momentum of s . The variable x^5 is related to s . In the Dirac theory K corresponds to the operator $\gamma^j(p_j - eA_j)$. The above classical equations correspond to a kind of generalized Dirac equation involving a fifth variable: $i(\partial\psi/\partial s) + \gamma^j(p_j - eA_j)\psi = 0$. The Dirac equation for the rest-mass m is obtained by taking $\psi = \exp[ims]\varphi$, φ depending only on the space-time co-ordinates x^j . The conformal geometry of the space-time seems to be involved in the theory of the mass-spectrum of the elementary particles.

The algebra G'_5 is associated to the geometry of the hyperspheres of the pseudo-euclidean space-time. Indeed, the equation of the hyperspheres of the n -dimensional space is $Y_\rho X^\rho = 0$, the Y 's being the so-called homogeneous co-ordinates of the hypersphere. The Y 's are not restricted by any condition. The hypersphere geometry leads to the introduction of the G_{n+2} of the dual linear spaces of vectors with components X^ρ and Y_ρ . The algebra G'_{n+1} is this G_{n+2} . The hyperplanes are also included in the present geometry as a

special kind of hypersphere. Our special choice of the hyperspherical co-ordinates corresponds to take as hyperspheres of indices $1, \dots, n$ the co-ordinate hyperplanes of the cartesian frame in the n -dimensional space.

The full development of the hypersphere geometry is given by the Lie geometry, in which the hyperspheres of the n -dimensional space are described by $n-3$ homogeneous co-ordinates Z satisfying a quadratic equation $\varphi(Z) = 0$. The basic group is now constituted by the linear transformations of the Z 's leaving invariant the equation $\varphi(Z) = 0$. We can take $Z_0 = Y_0$: $(Z_{n+2})^2 = -g^{jk}Z_jZ_k - (Z_{n+1})^2 - (Z_0)^2$ is the quadratic equation. We have now a Clifford algebra C_{n-3} associated to the quadratic form $\varphi(Z)$ and a G_{n+3} containing as a sub-algebra the above G'_{n+1} . *The transformations of the Lie geometry are not always point transformations. The Lie geometry may give a new two-valued variable in the case of the space-time, since it is associated to a G_7 .*

We have considered only algebras and quasi-algebras associated to groups depending on a finite number of parameters. The geometric groups depending on arbitrary functions, such as the group of the contact transformations, may also be important for the physics of the elementary particles, perhaps in connection with the theory of fields.

8. - Geometric algebras of complex spaces.

The geometric algebras we have been considering correspond to real spaces and may be taken over the real numbers. The quantum mechanics requires however algebras over the complex numbers. Thereby we are obliged to take our algebras over the complex numbers, so that we go over to complex spaces. *The geometry of the complex spaces requires both linear and anti-linear transformations, as well known from the projective geometry. The same happens in the affine geometry. The necessity of considering anti-linear transformations leads to an extension of the geometric algebras, as we shall now see.*

In a complex affine space we have, besides the V 's and U 's, conjugate contravariant and covariant vectors V^* 's and U^* 's, whose components transform by the conjugate linear transformations of those of the V_j 's and U_j 's for a change of the complex cartesian reference frame. We must therefore consider the basis of the I_j^* 's in the linear space whose elements are the V^* 's and the dual basis of the I^{*j} 's in the dual linear space of the U^* 's, with $\langle I_j^*, I^{*k} \rangle = \delta_j^k$. We shall denote by G_n^* the G -algebra associated to this pair of dual linear spaces. In order to treat conveniently the antilinear transformations of V 's into V^* 's and U 's into U^* 's, the algebras G_n and G_n^* may be fused into an algebra \bar{G}_n , by assuming that the generators (I) of G_n anti-commute with the generators (I^*) of G_n^* and taking the (I_j) , (I^j) , (I_j^*) , (I^{*j}) as generators of \bar{G}_n . \bar{G}_n is the G_{2n} associated to the direct sum of the linear

spaces of the V 's and V^* 's and to the direct sum of the U and U^* spaces. The \underline{L} quasi-algebra associated to those spaces will be denoted by \underline{L}_n .

It is important to notice that the above distinction of the V 's and V^* 's as vectors of different linear spaces is rather different from the treatment of points in a complex space in which the conjugate points belong to the same space. The introduction of the direct sum of two conjugate linear spaces is familiar from the theory of the spinors of the Lorentz group: the spinor space is the direct sum of the two conjugate spaces of the half-spinors. The two kinds of half-spinors are exchanged by a spatial reflection, but transform by conjugate linear transformations for a proper Lorentz transformation. The C_4 of the space-time may be considered as the \bar{G}_1 of a one dimensional complex space. This corresponds to the well known relations between the Lorentz group and the one-dimensional complex projective group.

The metric of a hermitian complex space is defined by a non-degenerate hermitian invariant form $h_{jk} V_1^j V_2^{*k} = (V_1, V_2)$. The unitary metric corresponds to $h_{jk} = \delta_{j,k}$. By means of h_{jk} we can associate to V the U^* of components $h_{jk} V^j$ and to V^* the U of components $h_{jk} V^{*k}$. *In the hermitian geometry it suffices to introduce the linear spaces of the V 's and V^* 's, because we can build the U 's and U^* 's with those two kinds of vectors, by means of the available h_{jk} .* The metric of a real space defined by the symmetric tensor g_{jk} can be extended into a hermitian metric of the complex space of the same number of complex dimensions, in which the former is embedded, by assuming that g_{jk} transforms as $U_j U_k^*$ for a complex linear transformation of the co-ordinates x^j . *The unitary metric is obviously the extension of the euclidean metric to the complex domain.*

We can now understand why G_n over the complex numbers is a Jordan-Wigner algebra. Let us write $I_k^\dagger = I h_{jk}$. The I_k^\dagger 's transform as the I_k^* for the linear transformations leaving invariant the h_{jk} 's, which constitute the h -unitary group. We can take the (I_j) 's and the (I_j^\dagger) 's as generators of G_n over the complex numbers and we have the commutation rules $[(I_j), (I_k)]_\pm = 0$, $[(I_j^\dagger), (I_k^\dagger)]_\pm = 0$, $[(I_j), (I_k^\dagger)]_\pm = h_{jk} 1_{G_n}$. *In the case of the unitary metric $h_{jk} = \delta_{j,k}$, $(I_j^\dagger) = (I^j)$ can be taken as the adjoint of (I_j) . The adjunction is an involution of G_n corresponding to the anti-polar transformation $V \rightarrow \sum (V^j)^* I_j^\dagger$ associated to the unitary metric.* In the case of G_n over the real numbers the adjunction becomes the transposition, which is an involution corresponding to the polar transformation $V \rightarrow \sum V^j I^j$, $U \rightarrow \sum U_j I_j$. Similar considerations can be applied to \underline{L}_n .

When the affine geometry of a complex space is considered, we cannot restrict \bar{G}_n and \underline{L}_n to G_n and \underline{L}_n . It may be necessary to extend the theory of the separable Hilbert spaces of the quantum mechanics into that of the associated complex affine spaces, at least in some cases. This leads to a duplication of the numbers of available states for the quanta in second quantization, since the second quantization of Jordan-Wigner and Dirac-Jordan-

Klein quasi-algebras will be replaced by the corresponding \bar{G}_∞ and \bar{L}_∞ . This duplication of the states corresponds to the introduction of a new two-valued variable of the quanta of the field.

The passage $G \rightarrow \bar{G}$ can be tentatively done in the case of the various G -algebras considered in the preceding sections. The G_1 of the scalars of Sect. 6 goes over into a \bar{G}_1 equivalent to the direct product of two Pauli spin algebras. *Thus we get the possibility of describing isotopic spin 0, $\frac{1}{2}$ and 1.* The G_4 of Sect. 6 goes over into a \bar{G}_4 equivalent to the direct product of four Dirac γ -algebras, which can be associated to four kinds of spin $\frac{1}{2}$ particles. *Thus we can introduce the electron, the μ -meson, the nucleon and the hyperon in our geometric-algebraic theory by replacing the G_5 of Sect. 6 by the corresponding \bar{G}_5 .* The passage from the G_6 of Sect. 7 to its \bar{G}_6 allows the inclusion of the neutrino and gives us a new two-valued variable. *The extension of the G -algebras into \bar{G} -algebras leads to an extension of the associated Duffin-Kemmer-Petiau algebras and gives room for the introduction of several types of bosons.*

The above considerations indicate that the elementary particles reflect not only the geometric properties of the real space-time but also those of a complex hermitian four-dimensional space-time. This is not surprising, because of the essential part played by the complex numbers in the quantum mechanics. The property of symmetry of the field of the complex numbers corresponding to the conjugation seems to matter not only in connection with the adjunction but also with the symmetry of the \bar{G} 's and \bar{L} 's.

9. - Vector analysis and wave equations.

We have discussed in this paper several kinds of vector calculus corresponding to G , C and D algebras. *There is a kind of vector analysis associated to each kind of vector calculus.* The C_4 vector analysis is characterized by the association of the symbolic covariant vector ∂ of components ∂_j to the symbol $\gamma_\partial = \gamma^j \partial_j$, which lies at the core of the Dirac theory of the spin $\frac{1}{2}$ particles. In a Duffin-Kemmer-Petiau vector analysis, we have the association of ∂ to $\beta_\partial = \beta^j \partial_j$. *The free-particle Dirac and Duffin-Kemmer-Petiau equations $(\gamma_\partial - im)\psi = 0$ and $(\beta_\partial - im)\psi = 0$ are obviously important geometric equations defining eigen- ψ 's of γ_∂ and β_∂ , respectively.* Those equations are actually generalizations of the Dirac and Duffin-Kemmer-Petiau equations, because ψ depends on a number of functions which may be different from the numbers of components involved in the ordinary wave equations.

In the case of the generalized Dirac equation, ψ denotes an element of C_4 depending on the co-ordinates x^j and involves in general 16 functions. *The generalized Dirac equation contains as particular cases, not only the ordinary Dirac equation, but also the Klein-Gordon and Proca equations for particles of*

mass m , the latter corresponding to the choices $\psi = \gamma^i B_i + B 1_{c_4}$ and $\psi = \frac{1}{2} \gamma^j \gamma^k B_{jk} + \gamma^i B_i$ (TIOMNO, private communication), B_{jk} denoting an antisymmetric tensor. When $m = 0$ and $\psi = \frac{1}{2} \gamma^j \gamma^k B_{jk}$, the generalized Dirac equation is equivalent to the Maxwell equations, B_{jk} being antisymmetric.

The above results indicate that both the quantum kinematics and the quantum dynamics deal with geometric properties of the space-time, the situation being, in principle, simpler in the relativistic quantum mechanics. The unity of matter, space and time in the macroscopic scale, discovered by EINSTEIN, seems to exist also in the microscopic scale. The fundamental symbol γ_{∂} combines the generators γ of the metric algebra of the space-time with the operators ∂ for the infinitesimal translations in an exceedingly simple way.

Let us consider now the vector analysis corresponding to G_n . ∂ is now associated to the symbol $(\partial) = (\mathbf{I})\hat{c}_j$. Let (Ψ) be any element of $G_n(P)$ depending on the x^j 's: $(\Psi) = \sum_p^{0 \dots n} (p!)^{-1} A_{j_1 \dots j_p} (P^{j_1 \dots j_p})$, the A 's being antisymmetric tensors. $(\partial)(\Psi)$ may be denoted by $\text{rot}(\Psi)$, because the left-multiplication of (Ψ) by (∂) corresponds to replace the tensors A by their rotationals. By means of the metric tensor, we can build the symbol $g^{jk}(\mathbf{I}_j)\hat{c}_k$, $g^{jk}(\mathbf{I}_j)\partial_k(\Psi)$ may be denoted by $\text{div}(\Psi)$, because the A 's are replaced by their divergences. The divergence is of course a metrical operator and the rotational an affine operator. We have the fundamental properties $\text{rot}^2 = 0$ and $\text{div}^2 = 0$. The laplacian operator for the (Ψ) 's is $\Delta = g^{jk}\partial_j\hat{c}_k 1_{\sigma_n} = [\text{rot}, \text{div}]_-$. The Dirac operator $\gamma_{\partial} = \text{div} + \text{rot}$. We see that the G_n vector analysis is more flexible than the C_n one, and richer too.

The generalized Dirac equation $(\gamma_{\partial} - im)\psi = 0$ can be conveniently included in the G_n vector analysis. Let us take $g_{jk} = \varepsilon_j \delta_{j,k}$, as always possible by a suitable choice of the basic vectors. It is easily seen that $(P^{j_1 \dots j_p}) = \gamma^{j_1} \dots \gamma^{j_p}(P)$, when all the j 's are different. We have therefore $(\Psi) = \psi(P)$ for any (Ψ) , ψ denoting an element of the C_n generated by the γ^j 's. The equation $(\gamma_{\partial} - im)\psi = 0$ is equivalent to $\text{rot}(\Psi) = (im - \text{div})(\Psi)$. When $m = 0$, the generalized Dirac equation becomes simply $\text{rot}(\Psi) = -\text{div}(\Psi)$. In the case of the space-time, the general solution of $(\gamma_{\partial} - im)(\Psi) = 0$ with $m \neq 0$ is obtained by means of the general solutions of the wave equations for scalar and pseudo-scalar, vector and pseudo-vector particles of mass m . The general solution of the ordinary Dirac equation is obtained from that of $(\gamma_{\partial} - im)\psi = 0$ by the right-multiplication of ψ by a suitable constant element of C_4 , which can be taken as $(1_{c_4} + i\gamma^4)(1_{c_4} + i\gamma^1\gamma^2)$, with $g_{jk}dx^jdx^k = (dx^1)^2 + (dx^2)^2 + (dx^3)^2 - (dx^4)^2$.

The vector analysis consists essentially in the theory of the direct product of C_n or G_n by \underline{L}_n . G_n is a geometric calculus for affine objects described by antisymmetric tensors and \underline{L}_n a geometric calculus for affine objects described by symmetric tensors. $G_n \times \underline{L}_n$ is a more complete geometric calculus, because

it allows to deal with objects described by general tensors. *This calculus leads to a generalization of the vector analysis, involving ordinary and symbolic functions.* In order to obtain a representation of $G_n \times \underline{L}_n$, it is convenient to consider the linear space $G_n \times \underline{L}_n(P)\{P\}$, whose elements χ are of the form $\chi = \sum_p (p!)^{-1} \cdot A_{j_1, \dots, j_p}(q)(I^{j_1}) \dots (I^{j_p})(P)\{P\}$, the $A(q)$'s denoting formal series of Hermite functions. χ can be associated to the generalized external differential expression $\sum_p (p!)^{-1} A_{j_1, \dots, j_p}(x)[dx^{j_1} \dots dx^{j_p}]$. $G_n \times \underline{L}_n$ is therefore a formalism for the theory of the external differentials, which allows the coefficients to be taken as ordinary or symbolic functions. Generalized external differential forms play an important part in the modern topology of differentiable manifolds (De Rham's currents). *The algebra of the relativistic wave equations is therefore related to the topology of the space-time as a differentiable manifold. The fact that the theory of the relativistic wave equations requires the passage to the quantum field theory suggests that the quasi-algebra of the quantum field theory is of topological nature.*

The generalized neutrino equation $\gamma_\partial(\Psi) = 0$ is particularly interesting. When $(p!)^{-1} A_{j_1, \dots, j_p}(P^{j_1, \dots, j_p}) = (\Psi)$, $\gamma_\partial(\Psi) = 0$ is equivalent to $\text{div}(\Psi) = 0$ and $\text{rot}(\Psi) = 0$. These equations, with $g_{jk} = \delta_{j,k}$, are well known from the theory of the harmonic integrals, where they characterize the harmonic differential forms. In the physical case, the laplacian is a \square -d'Alembertian, because of the indefinite metric of the space-time. The Maxwell equations correspond to $p = 2$. *In this case the equation $\gamma_\partial \psi = 0$ involves only the sub-algebra of C_4 generated by the Dirac α -matrices, $\alpha = \gamma^4 \Upsilon$, in three-dimensional vector notation. This sub-algebra is a C_3 , a reducible algebra isomorphic to the direct sum of two Pauli spin algebras.*

The above discussion of the generalized Dirac equation shows clearly how spinors can be obtained from sets of antisymmetric tensors. *In order to build spinors with antisymmetric tensors, it is necessary to have a formalism allowing the « addition » of tensors of different orders, such as the C and G algebras. The conventional tensor calculus does not allow such « additions ». Here lies the essential advantage of the geometric algebras with respect to the tensor calculus.* It is interesting to notice that the anticommutative Grassmann algebra gives already the possibility of « adding » antisymmetric tensors of different orders. The (Ψ) -space is actually $G_n^v(P)$, G_n^v denoting the Grassmann algebra of the covariant vectors generated by 1_{σ_n} and the (I) 's.

We used the relation $(P^{j_1, \dots, j_p}) = \gamma^{j_1} \dots \gamma^{j_p}(P)$ for $j_1 < \dots < j_p$, with $g_{jk} = \varepsilon_j \delta_{j,k}$. We have also $(P_{k_1, \dots, k_q}^{j_1, \dots, j_p}) = \gamma^{j_1} \dots \gamma^{j_p}(P) \gamma_{k_q} \dots \gamma_{k_1}$, with $j_1 < \dots < j_p$ and $k_1 < \dots < k_q$. G_n is generated by the γ_j 's and (P) . It suffices to introduce the extra generator (P) to pass from the metric algebra C_n to the affine algebra G_n .

REFERENCES

- [1] H. GRASSMANN: *Ausdehnungslehre* of 1862, *Gesammelte mathematische und physikalische Werke* (Leipzig, 1894-96).
- [2] M. SCHÖNBERG: *On the Grassmann and Clifford algebras I*, *Anais da Academia Brasileira de Ciencias*, **28** (1956).
- [3] M. SCHÖNBERG: *Summa Brasiliensis Physicae*, **1** (1947).

On the Possibility of Terrestrial Tests of the General Theory of Relativity.

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The recognition of the constant c as a truly universal constant is intimately connected with the development of the theory of relativity. In fact, the constancy of the velocity of light in vacuo for any system of inertia is a consequence of and a necessary condition for the validity of the principle of relativity itself. At this International Congress of Fundamental Constants, it may therefore be pertinent to review the experimental basis of this theory and to discuss the possibilities of new experimental verifications of relativity effects.

During the last fifty years, a large number of consequences of the special theory of relativity have been strikingly verified by experiments. Nevertheless, the experiments which give a direct verification of the *principle of relativity* of sufficient accuracy are limited to the two classical experiments by MICHELSON and IVES. It has been pointed out previously [1] that a slightly generalized Michelson experiment, where the interferometer is filled with a strongly refractive medium, would supply a further proof of the principle of relativity, which could not be explained away by an ad hoc hypothesis regarding the contraction of moving bodies. However, in view of the overwhelming experimental evidence in favour of the special theory, it seems hardly worthwhile to go through the trouble of repeating this rather difficult and costly experiment. It is therefore interesting to note that, as we shall see, some of the very accurate time measuring instruments constructed in recent years can be used for a new independent direct check of the principle of relativity.

In contrast to the special theory, the general theory of relativity cannot be considered satisfactorily verified by experiments. In spite of the fundamental difference in principles between Einstein's and Newton's theories of

gravitation, only the effects of large masses like that of the sun could so far give rise to measurable differences in the predictions of the two theories. Therefore, the three classical Einstein effects—the advance of the perihelion of Mercury, the gravitational shift of spectral lines, and the deflection of light in the gravitational field of the sun—have up to now been the only experimental tests of the theory, encumbered with all the uncertainties inherent in such astronomical measurements. Lately, this situation has radically changed due to the enormous development of experimental technique and the increased economic resources available for physical experiments. Although the gravitational effects on the earth are much smaller than in the space around the sun, it seems possible in a near future to obtain new tests of the general theory of relativity by terrestrial experiments which have the advantage over astronomical measurements of well defined experimental conditions. In the following, we shall discuss these possibilities.

The idea which suggests itself is an attempt at using «atomic clocks» to verify the relativistic formula for the rate of clocks placed at different potentials in a gravitational field. In our discussion, we shall confine ourselves to one type of atomic clocks, the «maser» [2], in which ammonia molecules are used as balance of the clock. The device utilizes a focused beam of excited ammonia molecules entering a cavity. For sufficiently high beam strength, the molecules can maintain a very monochromatic oscillation in the cavity due to microwave transitions in the molecules. The frequency of this oscillation determines the rate of the clock which, over long periods, has been shown to be accurate to at least one part in 10^{10} . Over shorter periods, of the order of one second, the accuracy is even considerably higher, up to 10^{-12} . A comparison of the rate of two masers is made by counting the beats of interference between the characteristic frequencies of the two masers.

Since the molecules enter the cavity with a certain velocity u , the frequency ν emitted by the molecules will, on account of the Doppler effect, depend on the direction of emission. The rate of the maser, or the characteristic frequency ν_m , will now be a certain mean value of the Doppler frequency, i.e.

$$(1) \quad \nu_m = \int \nu(\mathbf{e}) f(\mathbf{e}) d\Omega,$$

where \mathbf{e} is a unit vector in the direction of the photon emitted, and the weight function $f(\mathbf{e})$ depends on the geometrical arrangement of the apparatus [3].

Let us, to begin with, disregard the principle of relativity and calculate ν_m on the basis of the absolute ether theory. In this theory, we have approximately to the second order in the velocities [4]

$$(2) \quad \nu = \nu_0 \left[1 + \frac{\mathbf{e} \cdot \mathbf{u}}{c} + \frac{(\mathbf{e} \cdot \mathbf{u})^2}{c^2} + \frac{\mathbf{v} \cdot \mathbf{u}}{c^2} \right],$$

where \mathbf{u} is the velocity of the molecules in the laboratory system, while \mathbf{v} is the absolute velocity of the laboratory. Further, ν_0 is the proper frequency for $\mathbf{u} = 0$. By introduction of (2) into (1), we get for the characteristic frequency

$$(3) \quad \nu_m = \nu_0 \left[1 + g(u) + \frac{\mathbf{v} \cdot \mathbf{u}}{c^2} \right],$$

where $g(u)$ is the mean value of $\mathbf{e} \cdot \mathbf{u}/c + (\mathbf{e} \cdot \mathbf{u})^2/c^2$ and, thus, a function of the magnitude of \mathbf{u} only. However, on account of the scalar product term in (3), the rate of the maser should, according to (3), depend on its orientation with respect to the absolute velocity vector \mathbf{v} . In the actual maser, the majority of the molecules have a velocity $\mathbf{u} = 4 \cdot 10^4$ cm/s, and the absolute velocity \mathbf{v} of the laboratory may be put equal to the velocity of the earth in its orbit around the sun, i.e. $v = 3 \cdot 10^6$ cm/s. The relative change of the rate of the maser by a rotation through an angle of 180° should thus, according to the absolute ether theory, be of the order of 10^{-10} , an effect which it is quite possible to detect with the present accuracy of the maser. On account of the rotation of the earth around its axis, it is even not necessary to rotate the apparatus in order to detect the effect. If one uses two masers with opposite directions of the molecular beams, the effect in question should simply give rise to a diurnal variation of the relative rates of the two masers. On the other hand, according to the principle of equivalence and the principle of relativity, a rotation of the apparatus should *not* have any effect on the rate, as is seen at once if one introduces a local system of inertia at the space-time point in question for our description of the phenomena. Thus, if no diurnal variation of the rate is found, this may be regarded as a new check of the principle of relativity.

We shall now calculate the characteristic frequency of the maser according to the general theory of relativity. In an arbitrary gravitational field, we have instead of (2) the following exact formula for the Doppler effect (see Appendix A):

$$(4) \quad \nu = \nu_0 \frac{E_0}{E[1 - c'(\mathbf{p} \cdot \mathbf{e})/E]},$$

where E and \mathbf{p} are energy and momentum of the molecule in the gravitational field, and E_0 is the energy of the molecule at rest. Further,

$$(5) \quad c' = c \sqrt{1 + 2\chi/c^2},$$

where χ is the scalar gravitational potential, and ν_0 is the frequency emitted by a molecule at rest in the field. This frequency is connected with the proper

frequency $\tilde{\nu}_0$ of the molecule when placed at rest in a system of inertia by the formula (Eq. (A.19) in Appendix A)

$$(6) \quad \nu_0 = \tilde{\nu}_0 \sqrt{1 + 2\chi/c^2}.$$

Expanding E and p in powers of the velocity u , and keeping terms up to the second order only, gives

$$(7) \quad \nu = \nu_0 \left[1 - \frac{1}{2} \frac{u^2}{c'^2} + \frac{(\mathbf{u} \cdot \mathbf{e})^2}{c'^2} + \frac{\mathbf{u} \cdot \mathbf{e}}{c'} \left(1 + \frac{\mathbf{Y} \cdot \mathbf{u}}{c'} \right) \right],$$

which, by introduction into (1), gives the characteristic frequency ν_m . The exact value of ν_m will, of course, depend on the precise form of the weight function. If we assume that $f(\mathbf{e})$ is constant, independent of the direction, we get

$$(8) \quad \nu_m = \nu_0 \left[1 - \frac{1}{6} \frac{u^2}{c'^2} \right].$$

On the other hand, if $f(\mathbf{e})$ is assumed to be different from zero only for directions \mathbf{e} perpendicular to \mathbf{u} , we get

$$(9) \quad \nu_m = \nu_0 \left[1 - \frac{1}{2} \frac{u^2}{c'^2} \right].$$

In any case, the rate of the maser decreases with increasing energy of the molecules in the beam. This effect could in principle be checked by comparing the rate of two masers with different beam velocities, and this would effectively mean a new test of the relativistic Doppler formula. However, with the thermal velocities used so far, where $u = 4 \cdot 10^4$ cm/s at room temperature, the last terms in (8) and (9) are of the order of

$$(10) \quad \frac{u^2}{c^2} \approx 10^{-12},$$

which is perhaps somewhat too small to be measured with the present accuracy of the apparatus.

Neglecting terms of order $(u^2/c^2)((\chi_2 - \chi_1)/c^2)$, we get by (1), (6), and (7) for the ratio (τ_2/τ_1) of the rates of two identical masers placed at places with the potentials χ_2 and χ_1

$$(11) \quad \frac{\tau_2}{\tau_1} = \frac{\sqrt{1 + 2\chi_2/c^2}}{\sqrt{1 + 2\chi_1/c^2}} \approx 1 + (\chi_2 - \chi_1)/c^2.$$

If the two masers are connected by a cable or a wave guide, this effect can

in principle be measured by counting the beats between the characteristic frequencies of the two clocks. The formula (11) is in accordance with the general relativistic formula

$$(12) \quad d\tau = dt \sqrt{1 + 2\chi/c^2}$$

for the proper time $d\tau$ of an ideal standard clock at rest in a gravitational field as compared with the rate dt of the co-ordinate clocks. The equation (12), which is a simple consequence of the principle of equivalence, can also be derived by applying the laws of relativistic mechanics to the mechanism of a clock [5]. Under certain conditions, which are amply satisfied in the case of the oscillating ammonia molecules, (12) has been shown to be a consequence of the equations of motion of general relativity and in particular of the relativistic formula for the dependence of the rest mass m_0 of a particle on the gravitational potential

$$(13) \quad m_0 = \frac{\dot{m}_0}{\sqrt{1 + 2\chi/c^2}}.$$

Here, \dot{m}_0 is the mass of the particle when placed at rest in a system of inertia. An experimental verification of the equation (11) is therefore simultaneously a test of the relativistic formula (13) for the mass of a particle. For two masers, one at sea level, the other at a height h of 3 km, say, we get by (11) for the relative difference in rate

$$(14) \quad \Delta = \frac{\tau_2 - \tau_1}{\tau_1} = \frac{\chi_2 - \chi_1}{c^2} \approx \frac{|\text{grad } \chi| h}{c^2} \approx \frac{10^3 \cdot 3 \cdot 10^5}{9 \cdot 10^{20}} = \frac{1}{3} \cdot 10^{-12}.$$

Again, this effect is at the edge of what can be observed with the present accuracy of the available instruments, and we cannot gain much by climbing higher mountains.

Although it sounds somewhat fantastic at the moment, it may well be that, before clocks of considerably higher accuracy are constructed, it will be possible to use artificial satellites, in which case the effect in question can be made a thousand times bigger. As shown in Appendix B, we get for the relative difference in rate of two atomic clocks, one placed at the surface of the earth, the other in a satellite

$$(15) \quad \Delta = \frac{\tau_{\text{sat.}} - \tau_{\text{earth}}}{\tau_{\text{earth}}} = \frac{kM}{c^2} \left(\frac{1}{r} - \frac{3}{r_1 + r_2} \right),$$

where r , r_1 , and r_2 are the radius of the earth and the radii of the smallest and

largest distance of the satellite in its orbit around the earth, respectively. M is the mass of the earth and k is the gravitational constant. Hence,

$$(16) \quad \Delta = 0.7 \cdot 10^{-9} \cdot \left(1 - \frac{3r}{r_1 + r_2} \right).$$

The case of a circular orbit has already been discussed in detail by Dr. S. F. SINGER [6], who shows that the effect should be perfectly well observable by means of present day radio technique. The main point in SINGER's proposal is to use a counting method instead of a comparison of the frequencies of waves. Suppose the satellite clock has associated with it a scaler which counts its ticks and sends a short signal to the ground after each predetermined number of ticks. If the accumulation time or running time of the clock is sufficiently large, the detailed means of comparison between the satellite scaler and the ground clock becomes relatively unimportant. Also, if the errors are truly random, it is only a matter of time when the relativistic effect can be seen above the noise. According to (16) it will obviously be advantageous to use a highly eccentric satellite orbit $r_2 \gg r_1 \simeq r$, in which case the satellite clock has its maximum rate corresponding to $\Delta = + 0.7 \cdot 10^{-9}$. The communication signal could then, for instance, be sent each time the satellite has its closest distance to the earth.

The general relativistic effects considered so far may be regarded as consequences of general relativistic mechanics. Another characteristic action of the gravitational field is its influence on the velocity of propagation of radiation, which for instance is responsible for the deflection of light in a gravitational field. We shall now shortly discuss the possibility of measuring effects of this type by terrestrial experiments.

Any signal propagating through a medium at rest in a gravitational field, like that which exists in an earth-fixed system of reference, has a velocity w given by the general formula

$$(17) \quad w = \frac{c'}{(c/\bar{w}) + \boldsymbol{\gamma} \cdot \mathbf{e}},$$

(see Appendix C). Here, \mathbf{e} is a unit vector in the direction of propagation of the radiation, and \bar{w} is the velocity of the signal in a rest system of inertia for the medium in question. Further, c' is given by (5), and $\boldsymbol{\gamma}$ and χ are the vector and the scalar gravitational potential, respectively. For light going through a transparent medium of refractive index n , the velocity \bar{w} is, for instance, c/n , and c' is equal to the velocity of light in vacuo for a direction \mathbf{e} perpendicular to the vector potential $\boldsymbol{\gamma}$.

The difficulty in checking the formula (17) by terrestrial experiments lies

in the fact that only differences in the velocity (17) for different space points give rise to observable effects. This follows at once from the principle of equivalence; for inside a region of essentially constant potentials, we may treat the phenomena used in the experiment from the point of view of a local system of inertia, where the gravitational effects disappear. It is therefore clear that the experimental arrangement must cover large areas. Further, there is in general a danger that uncontrollable variations in the properties of the medium (i.e. in \hat{c}) will overshadow the weak effects due to the gravitational field. There is one arrangement, however, in which this latter difficulty is eliminated. Consider two signals which, starting from the same point P , are going along a closed loop, but in opposite directions. The time intervals T_+ and T_- needed for the signals to make one turn are then, according to (17),

$$(18) \quad T_{\pm} = \oint_{(\pm)} \frac{d\sigma}{w} = \oint \frac{c d\sigma}{c' w} \pm \oint_{(+)} \frac{\gamma \cdot e}{c'} d\sigma.$$

The time interval between the arrivals at P of the two signals after one turn is then completely independent of the properties of the medium traversed and equal to

$$(19) \quad \Delta t = 2 \oint_{(+)} \frac{\gamma \cdot e}{c'} d\sigma = \frac{2}{c} \oint_{(+)} a_{\sigma} d\sigma,$$

where the spatial vector \mathbf{a} is given by

$$(20) \quad \mathbf{a} = \gamma / \sqrt{1 + 2\chi/c^2}$$

and $a_{\sigma} = \mathbf{a} \cdot \mathbf{e}$ is the component of \mathbf{a} in the direction of the line element $d\sigma$ along the curve. By means of Stokes' theorem, which holds also in a non-Euclidean space, (19) may be written as a two-dimensional integral over a surface Σ delimited by the closed path of the signals

$$(21) \quad \Delta t = \frac{2}{c} \int_{\Sigma} (\text{curl } \mathbf{a} \cdot \mathbf{n}) dA,$$

where \mathbf{n} is a unit vector in the direction of the normal to the surface element with the area dA .

We can now introduce an earth-fixed system of co-ordinates (x, y, z, t) in which the covariant components of the vector potential are

$$(22) \quad \gamma_i = (\gamma_x, \gamma_y, \gamma_z) = \left(-\frac{\omega y}{c'}, \frac{\omega x}{c'}, 0 \right)$$

(see Appendix C). Here, ω is the angular velocity of the earth around its axis. By a simple calculation, one gets (Appendix C, Eqs. (C. 11)-(C 14))

$$(23) \quad \text{curl } \mathbf{a} = \mathbf{\Omega} + \mathbf{\Omega}_1,$$

where $\mathbf{\Omega}$ is a space vector lying in the direction of the axis of the earth and of the magnitude

$$(24) \quad |\mathbf{\Omega}| = \frac{2\omega}{c}.$$

Further $\mathbf{\Omega}_1$ is given by

$$(25) \quad \mathbf{\Omega}_1 = -\frac{2}{c^2}(\boldsymbol{\gamma}\mathbf{G}),$$

where

$$(26) \quad \mathbf{G} = -\text{grad } \chi$$

is the gravitational acceleration. Since $\boldsymbol{\gamma}$ is pointing to the east, and \mathbf{G} is pointing vertically downwards, the vector $\mathbf{\Omega}_1$ is pointing south and has the magnitude

$$(27) \quad |\mathbf{\Omega}_1| = \frac{2}{c^2}|\boldsymbol{\gamma}|G = \frac{2\omega}{c} \cdot \frac{rG}{c^2},$$

$$r = \sqrt{x^2 + y^2}.$$

If the loop is a plane curve, the surface Σ in (21) can be chosen to be a plane, and by (21) and (23) we get

$$(28) \quad \Delta t = \frac{2A}{c}[\mathbf{\Omega} \cdot \mathbf{n} + \mathbf{\Omega}_1 \cdot \mathbf{n}],$$

where A is the area enclosed by the loop. From (24) and (27) we see that $|\mathbf{\Omega}_1|$ is much smaller than $|\mathbf{\Omega}|$, by a factor

$$\frac{rG}{c^2} \approx \frac{6 \cdot 10^8 \cdot 10^3}{9 \cdot 10^{20}} \approx 10^{-9}.$$

If we neglect the second term in (28) entirely, we get for the phase difference ΔF of two waves of frequency ν after one turn in a horizontal plane

$$(29) \quad \Delta F = \nu \Delta t = \frac{4\nu\omega A \sin b}{c^2} = \frac{4\omega A}{\lambda c} \sin b,$$

where b is the geographical latitude. For visible light with $\lambda = 4 \cdot 10^{-5}$ cm we get

$$(30) \quad \Delta F \approx 10^{-9} A .$$

With an area of the order of $A = 1000 \text{ m}^2$, the phase difference will then be of observable magnitude. This first order effect was observed and verified by MICHELSON [7] in 1925 by means of a large interferometer.

However, unfortunately, this experiment cannot be regarded as a real test of the general theory of relativity, since the first order effect depends only on the « non-permanent » part of the gravitational field of the earth originating from the rotation of the earth around its axis. It is true that the principle of equivalence claims that there is no essential difference between such a type of gravitational field and the « permanent » fields due to the mass of the earth; but the fact remains that the formula (27) in first approximation is obtained also in the absolute ether theory, at least for light in vacuo. In fact, we get for the velocity of light in empty space in a system of reference which rotates with the angular velocity ω with respect to the absolute ether system

$$(31) \quad w = c [\sqrt{1 + (\mathbf{\Upsilon}' \cdot \mathbf{e})^2} - \mathbf{\Upsilon}' \cdot \mathbf{e}]$$

with

$$(32) \quad \mathbf{\Upsilon}' = \left(-\frac{\omega y}{c}, \frac{\omega x}{c}, 0 \right) .$$

To the first order in $\mathbf{\Upsilon}'$, (31) then leads to the formula (29). In order to obtain a real test of the general theory of relativity, it would be necessary to measure the effect due to the vector $\mathbf{\Omega}_1$ in (28), which depends on \mathbf{G} , i.e. on the « permanent » gravitational field as well as on the field originating from the rotation of the earth. This would require a 10^9 times larger area A . Even if it could be arranged so that the signals are making 100 turns instead of just one, the required diameter of the loop would have to be of the order of 100 km. In spite of the marvellous development of radar technique in recent years, it does not therefore seem possible in the foreseeable future to measure any truly relativistic effect of the gravitational field of the earth on the velocity of propagation of radiation.

Thus, it seems that the influence of gravitational fields on the rate of atomic clocks provides the only effects which lend themselves to a check by terrestrial experiments in the near future. On the other hand, a further development of the accuracy of these instruments is probably the only way to eventually checking the non-linear effects of general relativity, which are the really characteristic features of this theory, distinguishing it from the various linear theories of gravitation. However, the accuracy required to open up

this entirely new world is of the order of 10^{-18} , which is the order of magnitude of the non-linear terms in the expression for the rate of standard clocks. If such a high precision of the atomic clocks should ever be obtained, one would have to take into account a number of other effects, the largest of which is the influence of the gravitational field of the moon. In fact, the influence of this field on the quantity Δ in (14) is of the order of 10^{-17} . For two antipodal clocks on the earth, the relative difference in rate due to the gravitational field on the moon is even as large as 10^{-14} . On account of the rotation of the earth around its axis, this effect will obviously give rise to a diurnal variation of the relative rates of the clocks of corresponding magnitude.

APPENDIX A

Emission of photons from an atomic system moving in a gravitational field.

In an arbitrary system of space-time coordinates $(x^i) = (x^t, ct)$ with the four-dimensional interval

$$(A.1) \quad ds^2 = g_{ik} dx^i dx^k,$$

the dynamical action of the gravitational field is determined by the scalar potential χ and the vector potential γ_i defined by

$$(A.2) \quad g_{44} = -(1 + 2\chi/c^2); \quad \gamma_i = g_{i4}/\sqrt{-g_{44}}.$$

(Latin indices are running from 1 to 4, while Greek indices, which denote components of spatial vectors and tensors, are running from 1 to 3, only). Further, the influence of the gravitational field on the spatial geometry in the system of reference considered is described by the spatial metric tensor $\gamma_{\alpha\kappa}$ entering in the line element

$$(A.3) \quad d\sigma^2 = \gamma_{\alpha\kappa} dx^\alpha dx^\kappa; \quad \gamma_{\alpha\kappa} = g_{\alpha\kappa} + \gamma_\alpha \gamma_\kappa.$$

Hence,

$$(A.4) \quad ds^2 = d\sigma^2 - (c' dt - \gamma_i dx^i)^2$$

with c' given by Eq. (5) in the text.

In the following we shall only have to consider stationary fields where χ , γ and $\gamma_{\alpha\kappa}$ are time-independent. A particle, elementary or composite, which in a rest system of inertia has a mass \tilde{m}_0 will, when moving with the velocity \mathbf{u} in a gravitational field, have a mass m , momentum vector \mathbf{p} , and energy E

given by the following equations [8]:

$$(A.5) \quad \begin{cases} m = \tilde{m}_0 / [(\sqrt{1 + 2\chi/c^2} - \boldsymbol{\gamma} \cdot \mathbf{u}/c)^2 - u^2/c^2]^{\frac{1}{2}}, \\ \mathbf{p} = m\mathbf{u}, \\ E = mc'(c' - \boldsymbol{\gamma} \cdot \mathbf{u}). \end{cases}$$

Here, \mathbf{u} is the velocity vector with contravariant components $u^i = dx^i/dt$, $\boldsymbol{\gamma} \cdot \mathbf{u} = \gamma_i u^i$ is the scalar product of the vector potential $\boldsymbol{\gamma}$ and the velocity vector, and $u^2 = \gamma_{ik} u^i u^k$ is the square of the velocity. In a stationary gravitational field, the energy E is a constant of the motion for a freely falling particle. A simple calculation shows that E and $|\mathbf{p}|^2 = p_i p^i = m^2 u^2$ are connected by a similar equation as energy and momentum of a free particle in a system of inertia, viz.

$$(A.6) \quad |\mathbf{p}|^2 - (E/c')^2 = -\tilde{m}_0^2 c^2.$$

This follows at once from (A.5), noticing that m may be written

$$(A.7) \quad m = \tilde{m}_0 c / \sqrt{(c' - \boldsymbol{\gamma} \cdot \mathbf{u})^2 - u^2/c^2}.$$

The velocity of light w in the gravitational field (A.1)-(A.4) depends on the direction of propagation e and is equal to [9]

$$(A.8) \quad w = c' / (1 + \boldsymbol{\gamma} \cdot \mathbf{e}),$$

i.e.

$$(A.9) \quad w = c' - \boldsymbol{\gamma} \cdot \mathbf{w}; \quad \mathbf{w} = w\mathbf{e}.$$

If we let \mathbf{u} in (A.7) approach the velocity of light \mathbf{w} , the denominator goes to zero and we have to let \tilde{m}_0 go to zero also in order to get a finite value for the mass m . In this way we get from (A.5) and (A.9) for the momentum and energy of a photon in a gravitational field

$$(A.10) \quad \begin{cases} \mathbf{p} = m\mathbf{w} = m w \mathbf{e}, \\ E = m c' w. \end{cases}$$

Hence,

$$p = |\mathbf{p}| = E/c',$$

in accordance with (A.6) in the limit $\tilde{m}_0 \rightarrow 0$.

If ν is the frequency of the radiation to which the photon belongs we have for its energy and momentum

$$(A.12) \quad E = h\nu; \quad \mathbf{p} = \frac{h\nu}{c'} \cdot \mathbf{e},$$

where h is Planck's constant.

A photon travelling through a gravitational field may thus be treated as

a «freely falling» particle of rest mass zero. If the field is stationary its energy, and thus its frequency, is constant along the path. The red shift of spectral lines emitted at the surface of the sun is therefore, according to this theory, *not* due to a change of frequency of the light on its way to the earth (as in some of the popular explanations of this phenomenon), but rather to a difference in the energy levels of an atom when it is placed at different gravitational potentials.

Let us now consider a molecule in an excited state moving through a gravitational field with the velocity \mathbf{u} . When the molecule makes a transition to the ground state a photon is emitted, a process in which the total energy and momentum are conserved.

Let \dot{m}_0 , \mathbf{p} and E be the proper mass, momentum and energy, respectively, of the molecule before the process. They are connected by the equations (A.5) and (A.6). If \bar{m}_0 , $\bar{\mathbf{p}}$, \bar{E} are the corresponding quantities after the emission of the photon, we have

$$(A.13) \quad \mathbf{p} - \bar{\mathbf{p}} = \frac{h\nu}{c'} \mathbf{e}; \quad E - \bar{E} = h\nu.$$

Elimination of \mathbf{p} and E from the equations (A.13), (A.6), and the analogous equation

$$(A.14) \quad |\bar{\mathbf{p}}|^2 - (\bar{E}/c')^2 = -\bar{m}_0^2 c^2$$

gives after a simple calculation

$$(A.15) \quad \nu = \frac{(\dot{m}_0^2 - \bar{m}_0^2)c^2 c'^2}{2hE[1 - c'(\mathbf{p} \cdot \mathbf{e})/E]}.$$

If the initial velocity \mathbf{u} of the molecule is zero the frequency emitted is, according to (A.5) and (A.15),

$$(A.16) \quad \nu_0 = \frac{(m_0^2 - \bar{m}_0^2)c^2 c'^2}{2hE_0},$$

where

$$(A.17) \quad E_0 = m_0 c'^2 = \dot{m}_0 c^2 \sqrt{1 + 2\chi/c^2}$$

is the rest energy of the molecule at a place of gravitational potential χ . From (A.15) and (A.16) we get the formula (4), i.e.

$$(A.18) \quad \nu = \nu_0 \frac{E_0}{E[1 - c'(\mathbf{p} \cdot \mathbf{e})/E]}.$$

Further we get from (A.16), (A.17) and (5)

$$(A.19) \quad \nu_0 = \dot{\nu}_0 \sqrt{1 + 2\chi/c^2},$$

where

$$(A.20) \quad \bar{\nu}_0 = \frac{(\bar{m}_0^2 - \bar{m}_0^2)c^2}{2h\bar{m}_0}$$

is the frequency emitted when also χ is equal to zero, i.e. when the molecule is at rest in a system of inertia. (A.19) is identical with the equation (6). Expansion of E and \mathbf{p} in powers of the velocity \mathbf{u} leads at once from (A.18) to the expansion (7) used in the previous discussion.

APPENDIX B

Satellite problems.

Since the earth is falling freely in the gravitational field of the sun it is clear that we can introduce a system S of space-time coordinates (x, y, z, t) which at all times is a local system of inertia, for the centre of gravity of the system earth-moon with the spatial coordinates $x = y = z = 0$. In the linear approximation, we get for the interval in the space surrounding the earth

$$(B.1) \quad ds^2 = [1 - 2(\chi_1 + \chi_{\text{moon}})/c^2 + O(10^{-12})](dx^2 + dy^2 + dz^2) - \\ - [1 + 2(\chi_1 + \chi_{\text{moon}})/c^2 + O(10^{-16})]c^2 dt^2,$$

where

$$(B.2) \quad \chi_1(x, y, z) = -k \int \frac{\mu(x', y', z') dx' dy' dz'}{\sqrt{(x - x')^2 + (y - y')^2 + (z - z')^2}}$$

is the permanent scalar gravitational potential due to the mass distribution μ of the earth and χ_{moon} is the corresponding potential of the moon. Thus neglecting terms of the order 10^{-16} in g_{44} and terms of the order 10^{-12} in the remaining components of the metric tensor g_{ik} , the influence of the gravitational field of the sun has disappeared completely in S . This is a good approximation for distances from the centre of the earth of at least 10 times the radius of the earth, as is readily seen by actually performing the transformation from the system in which the sun is at rest to the system S which follows the motion of the earth.

For a spherical earth we would get

$$(B.3) \quad \chi_1 = -\frac{kM}{r}, \quad r = \sqrt{x^2 + y^2 + z^2},$$

and this approximation is sufficient for our purposes. At the surface of the

earth the order of magnitude of the potentials in (B.1) is

$$(B.4) \quad \chi_1/c^2 \approx 10^{-9}, \quad \chi_{\text{moon}}/c^2 \approx 10^{-14}.$$

As a first approximation we may neglect the weak field of the moon, and the gravitational field in S is then time-independent.

Now consider a standard clock placed on an artificial satellite circling around the earth.

Since the vector potential is zero in S , we get for the proper time τ of the clock [10], on account of (A.5),

$$(B.5) \quad d\tau = dt \sqrt{1 + 2\chi_1/c^2 - u^2/c^2} = dt \frac{\dot{m}_0}{m} = dt \frac{\dot{m}_0 c^2}{E} (1 + 2\chi_1/c^2),$$

where m_0 and E are the proper mass and the energy, respectively, of the satellite in its orbit. The factor $\dot{m}_0 c^2/E$ is a constant of the motion, and by means of the equations of motion the exact formula (B.5) allows us to calculate the increase $\Delta\tau$ in the reading of the clock for the time interval Δt between two positions of closest approach of the satellite and the earth. However, since the effect in which we are interested is small, we can replace the exact equations of motion by the corresponding approximate equations of Newtonian mechanics. If we introduce polar coordinates (r, φ) in the plane of the orbit, we have in this approximation

$$(B.6) \quad \frac{1}{2} (\dot{r}^2 + r^2 \dot{\varphi}^2) - \frac{kM}{r} = \frac{E}{m_0} - c^2 \equiv -\frac{B}{2},$$

$$(B.7) \quad r^2 \dot{\varphi} = C,$$

where B and C are constants of integration.

The first equation is obtained from (A.5) by expanding the energy in powers of χ_1/c^2 and u^2/c^2 and retaining only the terms linear in these quantities. The second equation is the usual angular momentum integral which is a consequence of the spherical symmetry of our problem. The equations (B.6), (B.7) differ from the corresponding exact equations only by terms which are 10^{-9} times smaller than the terms retained. By elimination of $\dot{\varphi}$ we get the radial equation of the Kepler motion

$$(B.8) \quad \dot{r} = \pm \frac{\sqrt{B}}{r} \sqrt{-r^2 + \frac{2kMr}{B} - \frac{C^2}{B}} = \pm \frac{\sqrt{B}}{r} \sqrt{(r-r_1)(r_2-r)},$$

where r_1 and r_2 , the radii of smallest and largest distances in the orbit, are connected with the constants of integration B and C by

$$(B.9) \quad r_1 + r_2 = \frac{2kM}{B}, \quad r_1 r_2 = \frac{C^2}{B}.$$

Hence

$$(B.10) \quad \frac{E}{\dot{m}_0 c^2} = 1 - \frac{B}{2c^2} = 1 - \frac{kM}{(r_1 + r_2)c^2}.$$

For the time interval Δt between two positions of closest approach we get from (B.8)

$$(B.11) \quad \Delta t = \frac{2}{\sqrt{B}} \int_{r_1}^{r_2} \frac{r dr}{\sqrt{(r-r_1)(r_2-r)}} = \frac{(r_1 + r_2)\pi}{\sqrt{B}} = \frac{\pi(r_1 + r_2)^{\frac{3}{2}}}{\sqrt{2kM}} [1 + O(10^{-9})],$$

where, in the last expression, the order of magnitude of the different terms neglected in the calculation is indicated by $O(10^{-9})$. In the same approximation we get from (B.5), (B.8), and (B.10) for the increase in the proper time of the satellite clock

$$(B.12) \quad \Delta\tau_{\text{sat.}} = \frac{m_0 c^2}{E} \int_0^{\Delta t} \left(1 - \frac{2kM}{c^2 r}\right) dt = \\ = \left(1 + \frac{kM}{(r_1 + r_2)c^2}\right) \Delta t - \frac{4kM}{c^2 \sqrt{B}} \int_{r_1}^{r_2} \frac{dr [1 + O(10^{-9})]}{\sqrt{(r-r_1)(r_2-r)}}.$$

Since the integral in the last term of (B.12) has the value π , this term may, by (B.10), (B.11), be written

$$(B.13) \quad - \frac{4kM(r_1 + r_2)^{\frac{3}{2}}\pi}{c^2 \sqrt{2kM}} [1 + O(10^{-9})] = - \frac{4kM\Delta t}{(r_1 + r_2)c^2} [1 + O(10^{-9})].$$

Hence,

$$(B.14) \quad \frac{\Delta\tau_{\text{sat.}} - \Delta t}{\Delta t} = - \frac{3kM}{(r_1 + r_2)c^2} [1 + O(10^{-9})].$$

A standard clock at rest on the surface of the earth has a velocity $r'\omega$ relative to S , where r' is the distance to the axis of rotation of the earth, and ω is the angular velocity in this rotation.

Hence

$$\frac{u^2}{c^2} \approx \left(\frac{r'\omega}{c}\right)^2 \approx 10^{-12} \approx \frac{kM}{c^2 r} \cdot 10^{-3}.$$

From the general formula (B.5) we therefore get for the rate of the earth clock

$$(B.15) \quad \frac{\Delta\tau_{\text{earth}} - \Delta t}{\Delta t} = \frac{\chi_1 - \frac{1}{2}r'^2\omega^2}{c^2} = \frac{\chi}{c^2} = - \frac{kM}{c^2 r} [1 + O(10^{-3})],$$

where $\chi = \chi_1 - \frac{1}{2}r'^2\omega^2$ is the scalar potential at the surface of the earth in

the earth-fixed system S_E introduced in Appendix C. From (B.14), (B.15) we get the formula

$$(B.16) \quad \frac{\Delta\tau_{\text{sat.}} - \Delta\tau_{\text{earth}}}{\Delta\tau_{\text{earth}}} = \frac{kM}{c^2} \left(\frac{1}{r} - \frac{3}{r_1 + r_2} \right),$$

i.e. the equation (15).

APPENDIX C

Propagation of radiation through a medium.

We shall now consider the propagation of radiation through a medium at rest in a system of reference S in which the gravitational field (A.1), (A.4) is stationary. If \dot{w} is the velocity of propagation of the radiation with respect to a system of inertia in which the medium is at rest, we have for the time-track of the signal

$$(C.1) \quad ds^2 = g_{ih} dx^i dx^h = d\dot{X}^i d\dot{X}^i - c^2 d\dot{T}^2,$$

where $\dot{X}^i = (\dot{X}^i, c\dot{T})$ are the space-time coordinates in a local rest system of inertia \dot{S} for the space-time point in question. Since $\dot{w}^2 = \sum_{i=1}^3 (d\dot{X}^i/d\dot{T})^2$ and $w^i = dx^i/dt$ are the contravariant components of the velocity of the signal in the gravitational field, (C.1) may be written, by means of (A.1)–(A.4),

$$(C.2) \quad w^2 - (c' - \gamma_i w^i)^2 = -c^2(1 - \dot{w}^2/c^2) \left(\frac{d\dot{T}}{dt} \right)^2,$$

where $w = d\sigma/dt = \sqrt{\gamma_{\alpha\beta} w^\alpha w^\beta}$ is the magnitude of the velocity of the signal in the gravitational field. Since the systems of reference S and \dot{S} are at rest with respect to each other at the space-time point P considered, the transformation connecting the space-time coordinates in S and \dot{S} must be such that

$$(C.3) \quad c d\dot{T} = -\gamma_i(P) dx^i + c \sqrt{1 + 2\chi(P)/c^2} dt = dt \left(c' - \gamma_i \frac{dx^i}{dt} \right),$$

where γ_i and χ in c' are the values of the potentials at the space-time point P . Combining (C.2) and (C.3) we get

$$w^2 - (c' - \gamma_i w^i)^2 = -(1 - \dot{w}^2/c^2)(c' - \gamma_i w^i)^2,$$

or

$$(C.4) \quad w = \frac{\dot{w}}{c} (c' - \gamma_i v^i).$$

Putting $w^i = w e^i$, where e^i are the contravariant components of a unit vector in the direction of propagation of the radiation, and solving with respect to w gives

$$(C.5) \quad w = \frac{c' w / c}{1 + (\dot{w}/c)(\boldsymbol{\gamma} \cdot \mathbf{e})} = \frac{c'}{(c/\dot{w}) + \boldsymbol{\gamma} \cdot \mathbf{e}},$$

which is the equation (17) of the text.

In an earth-fixed system $S_E: (x', y', z', t')$, connected with the coordinates of the system $S: (x, y, z, t)$ used in Appendix B by the transformation

$$(C.6) \quad \begin{cases} x = x' \cos \omega t' - y' \sin \omega t', \\ y = x' \sin \omega t' + y' \cos \omega t', \\ z' = z, \\ t' = t, \end{cases}$$

we have, disregarding the influence of the moon,

$$(C.7) \quad ds^2 = (1 - 2\chi_1/c^2)(dx'^2 + dy'^2 + dz'^2) - \\ - 2\omega y' dx' dt' + 2\omega x' dy' dt' - (1 + 2\chi_1/c^2 - r'^2\omega^2/c^2)c^2 dt'^2.$$

Here, ω is the angular velocity of the earth in its rotation around the z -axis. Thus, by (A.2), we get for the potentials in S_E

$$(C.8) \quad \chi = \chi_i - \frac{1}{2}r'^2\omega^2; \quad \gamma_i = \left(-\frac{\omega y'}{c'}, \frac{\omega x'}{c'}, 0 \right),$$

which is in accordance with (22) after dropping the primes on the coordinates in S_E . Further, the spatial metric tensor may be written

$$(C.9) \quad \gamma_{\alpha\kappa} = (1 - 2\chi_1/c^2)\delta_{\alpha\kappa} + \gamma_i \gamma_\kappa = (1 - 2\chi/c^2)\delta_{\alpha\kappa},$$

if we consistently neglect small terms of the order 10^{-12} . For the determinant $\gamma \equiv |\gamma_{\alpha\kappa}|$ we therefore get

$$(C.10) \quad \gamma = (1 - 2\chi/c^2)^3.$$

Using the general formulae defining the components of $\text{curl } \mathbf{a}$ and of the

vector product $\mathbf{a} \times \mathbf{b}$ of two vectors \mathbf{a} and \mathbf{b} [11]

$$(C.11) \quad \text{curl } \mathbf{a} = \frac{1}{\sqrt{\gamma}} \left(\frac{\partial a_3}{\partial x^2} - \frac{\partial a_2}{\partial x^3}, \frac{\partial a_1}{\partial x^3} - \frac{\partial a_3}{\partial x^1}, \frac{\partial a_2}{\partial x^1} - \frac{\partial a_1}{\partial x^2} \right),$$

$$(C.12) \quad (\mathbf{a} \times \mathbf{b})^i = \frac{1}{\sqrt{\gamma}} (a_2 b_3 - a_3 b_2, a_3 b_1 - a_1 b_3, a_1 b_2 - a_2 b_1),$$

it is easily seen that the curl of the vector (20) is of the form (23) with

$$(C.13) \quad \Omega^i = \frac{1}{(1 - 2\chi/c^2)^{\frac{1}{2}}(1 + 2\chi/c^2)} \left(0, 0, \frac{2\omega}{c} \right),$$

and Ω_i given by (25). In the expression for Ω_i we have consistently neglected a factor of the order $[1 + O(10^{-9})]$. For the norm of the vector Ω we get

$$(C.14) \quad |\Omega|^2 = \gamma_{\kappa} \Omega^i \Omega^{\kappa} = \\ = (1 - 2\chi/c^2) \frac{4\omega^2/c^2}{(1 - 2\chi/c^2)^3(1 + 2\chi/c^2)^2} = \frac{4\omega^2}{c^2} [1 + O(10^{-18})],$$

in accordance with the equation (24) in the text.

REFERENCES

- [1] C. MÖLLER: *The Theory of Relativity* (Oxford, 1952) (in the following quoted as C.M.), Chapter II, p. 64.
- [2] J. P. GORDON, H. J. ZEIGER and C. H. TOWNES: *Phys. Rev.*, **99**, 1264 (1955); K. SHIMODA, T. C. WANG and C. H. TOWNES: *Phys. Rev.*, **102**, 1308 (1956).
- [3] This information was given to me in a conversation with Professor C. H. TOWNES. I am grateful to Professor TOWNES for stimulating discussions on problems of general relativity in connection with the maser.
- [4] This formula follows at once from equation (23) in C.M., Chapter I, together with the relation $\mathbf{n} = \mathbf{e}(1 - \mathbf{v} \cdot \mathbf{e}/c) + \mathbf{v}/c$ which in the desired approximation gives the connection between the direction of the wave normal \mathbf{n} and the direction of propagation \mathbf{e} of the energy in the wave [see C.M., Chap. I, Eqs. (33)-(35)].
- [5] C. MÖLLER: *Dan. Mat. Fys. Medd.*, **30**, no. 10 (1955). See also *Report of the Relativity Conference in Bern* (1955).
- [6] S. F. SINGER: *Application of an Artificial Satellite to the Measurement of the General Relativistic «Red Shift»*, *Phys. Rev.*, **104**, 11 (1956). I am grateful to Dr. SINGER for the opportunity of seeing his manuscript prior to publication.
- [7] A. A. MICHELSON: *Phil. Mag.*, **8**, 716 (1904); *Astrophys. Journ.*, **61**, 137 (1925); A. A. MICHELSON and H. G. GALE: *Astrophys. Journ.*, **61**, 140 (1925).
- [8] C.M., Chap. X, Eqs. (12) and (22) or the Appendix of reference [5].
- [9] C.M., Chap. VIII, Eq. (70).
- [10] C.M., Chap. VIII, Eq. (99).
- [11] C.M., Appendix 5.

Causality in a Non-Local Field Theory and a Covariant Formulation of Interaction between Fields Based on the Introduction of a Universal Length.

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[Di questo lavoro, già pubblicato nel *Nuovo Cimento*, 5, p. 689 (1957), l'Autore ha voluto preparare per questi « Rendiconti » il riassunto che qui sotto riportiamo. (N.d.R.)]

Résumé. — One of the difficulties of non local field theories concerns the requirement of macroscopic causality. Another is the correct formulation of the non local interaction, which takes into account the necessity of referring the high energy and momenta (which must be cut-off or attenuated in some way) to the center of mass system (C. M.) of interacting incident particles (or to the C. M. of the bound state of a system). Our purpose is to make few remarks on the first problem and give an improved and more comprehensive formulation of the second. There is a well known incompatibility between the requirement of microscopic causality concerning the commutation relations and the basic assumptions of a non local interaction between two particles situated on a space like surface (2). We conclude that linear equations of motion and commutation relation for free fields have only an approximate validity. The macroscopic causality is violated (STUECKELBERG and WANDERS) and the convergence requirement is not fulfilled (C. BLOCH) if the form-factors introduced in the interaction-hamiltonian are functions only of the invariant intervals $(x' - x'')^2$. These conclusions do not apply to the cut-off operators suggested in some previous work by the author where these operators depend also on invariants formed with the total energy-momentum vector of the interacting incident particles. The simple form of the universal cut-off operator proposed in the present work is:

$$(1) \quad G(k, u) \equiv G(x) = 3 \sqrt{\frac{\pi}{2}} \alpha^{-\frac{3}{2}} I_{\frac{3}{2}}(\alpha),$$

where α is an invariant: $\alpha^2 = l^2[(k_v u^v) - k_\theta u^v]$; l is a universal constant

$$(2) \quad u_v = \frac{1}{m} P_v \quad P_v P^v = m^2 > 0$$

and $P_v = \sum_r p_v^{(r)}$ is the total energy momentum vector of the incident particle in the scattering problem, or is the total energy momentum of the dressed particle in the Heisenberg representation of the state of an elementary particle, or is the energy-momentum of the bound state. In all these cases the vector u_v is used in order to give the possibility of separating space and time components in the C M system of reference where u and α^2 assume the simple form:

$$u = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad \alpha^2 = l^2(K_1^2 + K_2^2 + K_3^2).$$

The choice (1), (2) of the G -operator corresponds to a form factor which in the C M system has a constant value inside a 3-dimension sphere: $x_1^2 + x_2^2 + x_3^2 \leq l^2$ and vanishes outside. If one uses the second quantization in the calculation of S matrix, then the G -operators are introduced into the interaction hamiltonian in such a way that one G -operator is associated with every creation and destruction operator of the interacting fields (also in the virtual states). Since all fields are interacting, more general interaction hamiltonians are necessary to describe high energy events and multiples production. In this theory all the renormalization constants are finite and the difference between renormalized and unrenormalized charges and masses is in principle observable. The interpretation of the significance of the cut-off operator G can be stated as follows. In C M system the statistical weight of a non degenerated state of a particle is equal to G^2

$$\text{if } K \rightarrow 0, G^2 \rightarrow 1; \quad \text{if } K \rightarrow \infty, G^2(\alpha) \sim \frac{\cos^2 \alpha}{\alpha^4}.$$

This theory introduces in a natural way non local fields depending on additional internal parameters (continuous + discontinuous). A detailed account of the proposed formalism containing the theory of multiple production in high energy collision is in press.

La costante di accoppiamento della interazione mesone nucleone.

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[Gli Autori hanno in preparazione un lavoro di rassegna sull'argomento indicato dal titolo di questo scritto. Della comunicazione presentata al Congresso riportiamo pertanto solo un breve riassunto da loro preparato. {N.d.R.}]

Riassunto. — Negli ultimi anni la nostra conoscenza sperimentale dei fenomeni riguardanti l'interazione fra mesoni π e nucleoni si è enormemente accresciuta. Benchè non si disponga ancora di uno schema teorico generale che spieghi in modo soddisfacente tutti i fenomeni fisici nei quali questa interazione gioca in modo preponderante, è stato tuttavia possibile recentemente ottenere previsioni teoriche in discreto accordo con i dati sperimentali. Nella presente relazione si discute se, allo stato attuale delle nostre conoscenze, sia possibile caratterizzare l'interazione mesone-nucleone con una costante fondamentale, la cosiddetta costante d'accoppiamento, il cui valore possa essere determinato univocamente facendo uso solo dei dati sperimentali e di alcune ipotesi teoriche generali sul campo mesonico, escludendo completamente il ricorso ad approssimazioni matematiche di dubbia validità.

Dopo aver svolto alcune considerazioni generali sul significato di costante di accoppiamento nella moderna teoria dei campi prendendo l'esempio più semplice e più noto dell'elettrodinamica, si espongono alcuni teoremi che permettono di esprimere sezioni d'urto per processi che coinvolgono mesoni al limite di massa zero in funzione della costante di accoppiamento rinormalizzata f^2 , e si discute in che modo si possano estra-

polare tali risultati per valori fisici dell'energia del mesone. In particolare ci si sofferma sulle determinazioni di f^2 per la teoria mesonica relativistica basate rispettivamente sul teorema di Kroll e Rudermann (esperienze di fotoproduzione) e sulle regole di dispersione (esperienze di scattering). Dopo aver discusso l'attendibilità di tali determinazioni si illustra la determinazione della costante di accoppiamento del modello di sorgente fissa basata sulle relazioni di Low, esaminando le ragioni dell'interesse che questo procedimento presenta.

Il fatto che i valori di f^2 ottenuti, in modi diversi, partendo da ipotesi differenti sull'interazione fondamentale pione-nucleone non differiscono fra loro di molto, ci sembra indicare che, anche in assenza di una descrizione matematicamente soddisfacente di tale interazione, essa sia caratterizzata fisicamente da un'unica costante dell'ordine di grandezza $f^2/\hbar c = 0.08$.

Las Constantes Universales de la Física.

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1. - Leyes y ecuaciones.

Lo que caracteriza la física moderna como ciencia positiva es que se basa en medidas. De un fenómeno natural cualquiera pueden dar los poetas bellas descripciones que pueden satisfacer a quienes se conformen con lo que es apprehendido directamente por los sentidos y con las ideas que ello sugiera. Pero el físico pretende descubrir leyes que se expresen en forma matemática, lo que exige, ante todo, definir la operación de medir y averiguar qué cosas son susceptibles de medida.

Toda teoría física se basa en cierto número de leyes fundamentales de las que, por los métodos de la lógica matemática se deducen las leyes derivadas. Es de notar que la distinción entre una y otra especie de leyes es, hasta cierto punto, convencional, pues hay libertad en la elección de las leyes, independientes entre sí, sobre las que se basa una teoría dada.

Es un hecho, que cualquiera puede comprobar, que es posible elegir las leyes fundamentales de modo que consistan en relaciones de proporcionalidad entre potencias determinadas de cantidades cuya medida ha sido previamente definida. Tales relaciones pueden enunciarse sin hacer referencia a ningún sistema particular de unidades. Así, al decir que un cuerpo sometido a una fuerza constante ejecuta un movimiento en el que los espacios son proporcionales a los cuadrados de los tiempos, se afirma algo que cualquiera puede comprobar utilizando unidades cualesquiera para medir las longitudes y los tiempos.

En los libros de Física que proceden metódicamente, el enunciado verbal de cada ley va seguido de una ecuación algébrica que se considera como la expresión cabal y completa de dicha ley. Aun cuando no se diga expresamente, la sustitución del vocablo «proporcional» por el signo de igualdad indica que

las cantidades han sido reemplazadas por sus medidas. Admitiremos, pues, que *las ecuaciones físicas relacionan las medidas de las cantidades que en ellas interviene*. Los símbolos, por tanto, representan números.

2. - Constantes características y constantes universales.

Al pasar de la relación de proporcionalidad entre cantidades a la ecuación entre medidas, será preciso, en general, introducir un factor de proporcionalidad, C , para tomar en consideración la arbitrariedad en la elección de unidades. Según esto, la expresión general de una ley fundamental será de la forma:

$$y = C x_1^{\alpha_1} \dots x_n^{\alpha_n},$$

y, una vez fijadas convencionalmente las unidades con que deben medirse las magnitudes que figuran en el fenómeno en cuestión, bastará medir todas ellas en un caso particular para hallar el valor de C :

$$(1) \quad C = \frac{y}{x_1^{\alpha_1} \dots x_n^{\alpha_n}},$$

que dependerá, en general, de las unidades adoptadas. La expresión (1) puede considerarse como la definición de C , que adquiere con ello la cualidad de *magnitud secundaria*, pues se encuentra en el mismo caso que aquellas magnitudes, como la velocidad, la densidad, etc., cuya medida no puede obtenerse sino a partir de su ecuación de definición.

Al calcular el factor de proporcionalidad correspondiente a una ley fundamental, pueden presentarse dos casos, según que el resultado dependa o no de la naturaleza del cuerpo con que se opera. En el primer caso, dicho factor se llama *constante característica*. En el segundo, que es el que nos interesa, el tal factor es una *constante universal*.

He aquí una lista de leyes fundamentales con sus respectivas constantes universales:

1) *Constante de la gravitación*. - Aunque no se diga expresamente, las leyes de la gravitación son dos, a saber:

Los cuerpos se atraen en razón directa de su masa gravitatoria y en razón inversa del cuadrado de su distancia.

La masa gravitatoria es proporcional a la masa inercial.

Cada una de estas leyes se expresa mediante una ecuación entre medidas con su respectivo factor de proporcionalidad, que adquiere distinto valor según sean las unidades que se adopten para la distancia, la fuerza y para ambas

especies de masa. Pero, eligiendo convenientemente las unidades, por ejemplo utilizando el sistema cegesimal, ocurre que la primera vale 1, y resulta:

$$f = G \frac{m_i m_i'}{d^2}; \quad m_g = \sqrt{G} m_i,$$

donde m_g es la masa gravitatoria, m_i la masa inercial y G la constante de la gravitación.

2) *Equivalente mecánico del calor.* — Entre el calor absorbido, Q , por un sistema en una transformación cíclica, y el trabajo producido, W , existe la ecuación

$$W = JQ,$$

donde J es el equivalente mecánico del calor, cuyo valor sólo depende de las unidades con que se miden W y Q .

3) *Constante de Avogadro.* — En todo cuerpo, el número de moles, n , es proporcional al número de moléculas N :

$$N = N_A n,$$

donde N_A es la constante de Avogadro, cuyo valor sólo depende de la unidad que se adopte para medir masas.

4) *Constante de Boltzmann.* — En todo sistema formado por gran número de elementos, la energía, $\bar{\varepsilon}$, que por término medio corresponde a cada grado de libertad, es proporcional a la temperatura absoluta, θ :

$$\bar{\varepsilon} = \frac{1}{2} k \theta,$$

donde k es la constante de Boltzmann, que sólo depende de las unidades con que se midan la energía y la temperatura.

5) *Constante de Planck.* — En todo proceso periódico de frecuencia ν , la energía sólo puede experimentar cambios que sean múltiplos enteros de

$$\Delta \varepsilon = h \nu,$$

donde h es la constante de Planck.

6) *Velocidad de la luz.* — A todo aumento de energía corresponde un aumento de masa (inercial) dado por la ley de Einstein:

$$\Delta \varepsilon = c^2 m.$$

donde c es una constante universal que, con sistemas convenientes de unidades, el cegesimal por ejemplo, coincide con la medida de la velocidad de la luz en el vacío.

7) *Constantes del vacío.* — Algunas constantes específicas conservan un valor finito cuando se miden en el vacío. Una de ellas es la velocidad de la luz, de que ya hemos hablado. Las otras dos son la permeabilidad eléctrica, ϵ_0 y la permeabilidad magnética, μ_0 , cuyas ecuaciones de definición son:

$$D = \epsilon_0 E ; \quad B = \mu_0 H .$$

Ambas permeabilidades son, desde luego, constantes características de cada sustancia, y dependen de la presión y de la temperatura. Pero, como es natural, esta dependencia no existe cuando se trata del vacío, por lo que ϵ_0 y μ_0 deben ser incluidas entre las constantes universales.

8) *Constante dinámica.* — La primera ley de Newton admite un factor de proporcionalidad:

$$C = \frac{f}{ma} ,$$

que no ha recibido nombre ni símbolo. Su valor depende, exclusivamente, de las unidades que se elijan para medir la fuerza, la masa ó la aceleración, por lo que debe ser considerado como una constante universal.

9) *Constante electromagnética.* — En virtud de la ley de Laplace, todo elemento de corriente está sometido a una fuerza que es proporcional a la intensidad, I , a la longitud, dl , y a la proyección del vector magnético, B , sobre el plano normal a dl . Con la notación vectorial:

$$df = \gamma [dl \cdot B] I ,$$

donde γ es la constante electromagnética, que depende tan sólo de las unidades que se elijan para medir las magnitudes que figuran en esta expresión.

3. — Otras constantes universales.

Cualquier monomio formado con constantes universales será una nueva constante universal. Algunas tienen nombre, como las de Wien, Stefan, la constante de los gases, $R = kN_A$, y el faraday, que es el producto de la constante de Avogadro por la carga del electrón. También esta última magnitud, juntamente con la carga y la masa de las distintas partículas elementales,

deben considerarse como constantes universales, ya que tienen valores numéricos constantes en cuanto se fijan las respectivas unidades de medida.

4. — Opiniones acerca de las constantes universales.

Para ponderar la importancia de las constantes universales bastará decir que toda teoría física se ha iniciado con el descubrimiento de una nueva ley con su respectiva constante universal, y que la teoría se considera consolidada cuando, al medir la constante, se obtiene siempre el mismo número, cualquiera que sea el observador, el lugar y el tiempo en que se efectúa la medida, y el fenómeno particular que se reproduzca. Esta constancia, según PLANCK, permite afirmar que, en contra de la filosofía positivista, existe una realidad exterior, por lo que la Física tiene un propósito bien definido.

Las constantes universales tienen un carácter desconcertante. Aparecen en las leyes universales sin haber sido definidas previamente, ni cualitativa ni cuantitativamente. No son atributos de cada cuerpo, variables de uno a otro, lo cual hace que no sean magnitudes, pues se presentan siempre con igual cuantía, y decir que en otros universos pudieran tener otro valor es convertir la física en una mala metafísica. Como no existe sino un ejemplar de cada una, habrían de ser, si fuesen magnitudes, unidades de sí mismas, y su valor sería siempre el número 1. No son números puros, porque su valor depende de las unidades que se adopten para medir las magnitudes que concurren con ellas en las respectivas ecuaciones. Finalmente, su existencia es en cierto modo precaria, pues la que hemos llamado constante dinámica no se encuentra en ningún libro de Física; el equivalente mecánico del calor, al que se dedicaban extensos capítulos en los libros de comienzo de siglo, ha desaparecido totalmente de los libros modernos; las constantes del vacío, ϵ_0 y μ_0 , que no se encuentran en los tratados clásicos, empiezan a aparecer en los contemporáneos; con la adopción del sistema de Giorgi fenece la constante electromagnética, que por intervenir con variados exponentes en las fórmulas las convertía en verdaderos rompecabezas.

Parece plausible adoptar las unidades de modo que la constantes universales adquieran el valor 1, con lo que desaparecerían de las fórmulas. Pero como no se dispone de suficiente número de unidades arbitrarias, cada autor puede suprimir las constantes universales que menos le agraden, y por eso aparecen a diario trabajos en los que, con tal o cual poda de constantes, se pretende dar cierto sentido esotérico a determinadas leyes físicas.

Hay físicos, y muy distinguidos, que opinan que las constantes universales pueden utilizarse a modo de comodines para atribuir a alguna magnitud la dimensión que más convenga, y por eso no se ha llegado a un acuerdo acerca

de si la temperatura es una magnitud dimensionalmente independiente y, de no serlo, cual debería ser su fórmula dimensional.

Poco importaría esta discrepancia de criterios a no ser porque el planteo de cualquier problema de Análisis dimensional requiere decidir previamente qué constantes universales han de conservarse y cuáles pueden suprimirse. El mismo teorema de pi resulta inútil sin tal decisión. Es forzoso, por tanto, sentar una norma que permita decidir qué constantes universales son imprescindibles y cuáles son superfluas. En la pesquisa de esta norma hemos andado durante muchos años, hasta encontrar una fórmula sencilla que, puesta a prueba en problemas de Análisis dimensional tomados de los diversos capítulos de la Física, conduce siempre a resultados satisfactorios. Pero antes de enunciar dicho criterio necesitamos dar una definición.

5. – Magnitudes inseparables.

Si se examina la lista de ecuaciones fundamentales en que intervienen constantes universales se puede observar que se dividen en dos grupos. En el primero, que es el más numeroso, se encuentran las ecuaciones que relacionan entre sí dos magnitudes. El segundo está constituido por ecuaciones en que intervienen tres o más magnitudes y en él figuran tan sólo dos constantes universales, la constante dinámica y la constante electromagnética.

Entre las constantes del primer grupo destaca el equivalente mecánico del calor, J , que relaciona dos magnitudes, el calor y el trabajo que, si bien son cosas distintas, pueden transformarse una en otra, estando el tránsito regido por un principio de conservación.

Las restantes ecuaciones del primer grupo tienen un rasgo común. Relacionan *magnitudes inseparables*, esto es, magnitudes tales que la presencia de una de ellas en un objeto lleva consigo la presencia de la otra en el mismo objeto de tal manera que, a cuantías iguales de la primera corresponden cuantías iguales de la segunda. Así ocurre que, si se emplea un sistema coherente de unidades, por ejemplo el de Giorgi:

1) *Todo cuerpo que tenga un gramo de masa inerte, posee \sqrt{G} unidades de masa gravitatoria.*

2) *Donde haya un mol de un cuerpo cualquiera ha de haber un número de moléculas igual a la constante de Avogadro.*

3) *Allí donde la temperatura absoluta valga un grado, ha de haber gran número de partículas cuya energía media por grado de libertad sea igual a la mitad de la constante de Boltzmann.*

4) *Toda partícula que posea la unidad de energía cinética lleva asociado un fenómeno periódico cuya frecuencia es igual a la inversa de la constante de Planck.*

5) Si la energía de un cuerpo aumenta en una unidad, su masa inercial experimenta un aumento igual a la inversa del cuadrado de la velocidad de la luz.

6) En cualquier punto del vacío donde haya un campo eléctrico de intensidad unidad ha de haber un poder electrizante, (inducción electrostática), igual a la permeabilidad eléctrica del vacío.

7) En todo punto de vacío donde exista la unidad de inducción magnética, B , ha de haber un poder imanador H igual a la inversa de la permeabilidad magnética del vacío.

6. - Criterio para decidir cuales son las constantes universales ineludibles.

Son ineludibles las constantes universales que relacionan dos magnitudes inseparables, y superfluas todas las demás.

Según esto, y teniendo en cuenta que, en virtud de la ley de Maxwell es $c^2 = 1/\epsilon_0\mu_0$, sólo quedan en la Física actual seis constantes universales, que son: la de la gravitación, la de Avogadro, la de Boltzmann, la de Planck, la velocidad de la luz y la permeabilidad eléctrica del vacío.

Admitiendo la precedente proposición, se puede desarrollar el Análisi dimensional de un modo preciso, pues queda determinada sin ambigüedad la fórmula dimensional de cada magnitud. Además, se obtiene con su auxilio la solución correcta en todos los casos en que es conocida la solución exacta, según hemos hecho ver en un libro recientemente publicado [1].

7. - Del número de constantes universales independientes entre sí.

El universo está constituido por corpúsculos (electrones, protones, neutrones, etc.) que se caracterizan por su masa y por su carga eléctrica. A las diversas especies de corpúsculos corresponden masas diversas, pero sólo se conoce una carga elemental, la del electrón. Estas cantidades pueden considerarse como constantes universales, y ellas, juntamente con las constantes universales propriamente dichas (o sea con los factores de proporcionalidad que figuran en las ecuaciones fundamentales), son los sillares con que han de construirse las teorías físicas.

El análisis dimensional permite afirmar que, en cada teoría, el número de constantes universales dimensionalmente independientes no puede exceder de la multiplicidad de la base respectiva. Veremos, además, que siempre puede formarse una base con constantes universales exclusivamente, de donde resulta que cualquier otra constante habrá de ser función monomía de las que se tomen para formar la base. Las constantes universales, por consiguiente, pueden con-

siderarse como vectores en un espacio con tantas dimensiones como valga la multiplicidad de la base, esto es, cinco en el caso más general. En consecuencia, *no puede haber más de cinco constantes universales que sean dimensionalmente independientes.*

G. BECK [2] se ha ocupado en averiguar la conexión que debe existir entre las constantes universales, planteando correctamente la cuestión y haciendo ver su alcance teórico. Pero parte de la afirmación gratuita de que la base dimensional ha de estar constituida por las tres magnitudes longitud, masa y tiempo, por lo que sus consideraciones, muy ingeniosas por cierto, acerca del número de constantes universales dimensionalmente independientes carecen de fundamento. El problema en cuestión debe plantearse por separado en cada capítulo de la física, pues ocurre que son diferentes las multiplicidades de las respectivas bases dimensionales.

En la Mecánica cuántica y relativista bastan tres magnitudes básicas, que pueden ser: la masa, m , de una partícula elemental cualquiera, la velocidad de la luz y la constante de Planck, pues es fácil ver que son dimensionalmente independientes. Cualquier monomio formado con estas tres constantes universales será una nueva constante universal de naturaleza mecánica, y podremos formarla de modo que tenga una fórmula dimensional cualquiera. Si, por ejemplo, se trata de calcular una longitud o un tiempo en un problema mecánico en que intervengan tan sólo partículas de masa m , el Análisis dimensional da como solución dos nuevas constantes universales, a saber:

$$l_0 = C_l \frac{h}{mc}; \quad t_0 = C_t \frac{h}{mc^2}.$$

Los números puros C_l et C_t quedan indeterminados, pero si hubiere alguna razón para que no fuesen menores que uno, resultaría que en el problema en cuestión no podrían intervenir longitudes ni duraciones inferiores a h/mc y h/mc^2 , respectivamente. Con protones o neutrones, por ejemplo, resulta:

$$l_0 = 1.3309 \cdot 10^{-13} \text{ cm}; \quad t_0 = 4.43966 \cdot 10^{-24} \text{ s}.$$

La constante de la gravitación es de índole puramente mecánica, por lo que podrá igualarse a una expresión monomía en que figuren m , c , h . En efecto:

$$G = \pi_1 \frac{hc}{m^2}.$$

El valor del número puro π_1 depende de la partícula que se considere, y crece desde el electrón hasta el protón pasando por la ya larga serie de mesones. En todo caso, resultan números muy pequeños, a los que, por ahora, no se puede atribuir ningún significado.

En electromagnetismo hay que ampliar la base con una nueva constante, que puede ser la carga elemental, e . En consecuencia, cualquier otra constante universal ha de poderse igualar a un monomio en que figuran estas constantes. He aquí dos ejemplos:

$$\varepsilon_0 = \pi_2 \frac{e^2}{ch}; \quad \mu_0 = \pi_3 \frac{h}{e^2 c}.$$

El número puro π_2 , que figura en la expresión de la constante dieléctrica del vacío, está relacionado con la *constante de estructura fina* de Sommerfeld, que en el sistema electrostático vale:

$$\alpha = \frac{2\pi e^2}{ch} = 7.29 \cdot 10^{-3},$$

al paso que, con la base completa es:

$$\alpha = \frac{e^2}{2\varepsilon_0 ch} = 7.29 \cdot 10^{-3},$$

y, por consiguiente:

$$\pi_2 = \frac{1}{2\alpha} = 68.5.$$

Finalmente, en Termodinámica hace falta otra constante universal en la base, constante que ha de figurar en alguna ley en que intervenga la temperatura, y puede ser la constante de Boltzmann.

8. — Los números universales.

En la Geometría de EUCLIDES, la razón entre la circunferencia y el diámetro, cuando ambas magnitudes se miden con una misma unidad, es un número puro, el número π , que puede considerarse como una constante de dimensión nula propia del espacio euclídeo.

En Física se manejan constantes universales con las que es posible formar monomios de dimensión nula, los cuales serán números puros y pueden llamarse números universales. Tales son, por ejemplo, los números puros π_1 , π_2 y π_3 que hemos hallado en el apartado anterior.

Mucho se ha especulado acerca del significado de estos números universales. FINKELBURG [3], dando por supuesto que sólo hay una longitud universal, el radio del nucleón ($r_0 = 1.31 \cdot 10^{-13}$ cm), dos masas elementales, la del electrón y la del protón, y tomando en cuenta la carga elemental y las

constantes universales c , ε_0 , G y h , deduce que hay cuatro números universales:

$$\pi'_1 = \frac{m_0}{m_p} = 1837; \quad \pi'_2 = \frac{h}{m_p c r_0} \sim 1; \quad \pi'_3 = \frac{e^2}{\varepsilon_0 h c} = 14.58 \cdot 10^{-13};$$

$$\pi'_4 = \frac{e^2}{m_0 m_p \varepsilon_0 G} = 2.28 \cdot 10^{39}$$

y como comentario agrega.

«A pesar de las agudas sugerencias de EDDINGTON y de otros, falta una teoría que explique satisfactoriamente la razón de ser de estas constantes de dimensión nula. Ni siquiera hay unanimidad acerca de cómo ha de abordarse la cuestión con posibilidades de éxito. Es de suponer que las mayores dificultades surjan al tratar de explicar cómo sale un número tan enorme como al π'_4 , $2.28 \cdot 10^{39}$, pues es inverosímil que tal número resulte de relaciones entre magnitudes atómicas. Esto ha sugerido la idea de considerarlo como prueba evidente de la conexión entre los datos astronómicos y los atómicos. Las consideraciones de EDDINGTON, DIRAC, JORDAN y otros servirán para aguzar el ingenio de quien trate de abordar el problema».

Desde nuestro punto de vista ocurre que pueden obtenerse infinidad de números universales, pues pueden combinarse de infinitos modos las constantes universales de manera que resulten monomios π , por lo que, *a priori*, resulta inaccesible el problema de calcular teóricamente todos ellos. En cambio, tiene sentido la siguiente cuestión: *Dadas cinco constantes dimensionalmente independientes, calcular todas las que se encuentran en los distintos capítulos de la Física.*

El Análisis dimensional afirma que cualquier constante universal ha de poder expresarse por un monomio en el que figuren tan sólo algunas de las constantes universales que se adopten como básicas, con lo que el problema se reduce a hallar el respectivo factor numérico.

Problemas de este tipo han sido ya resueltos mediante las modernas teorías, y así se sabe, por ejemplo, calcular las constantes de Stefan, de Wien, de Rydberg, etc., pero otros están por resolver. Falta, por ejemplo, una teoría que permita calcular las relaciones entre las masas de las distintas partículas elementales; la constante de la gravitación en función de una masa elemental y de las constantes c y h ; las permeabilidades del vacío en función de c , ε_0 , etc.

REFERENCIAS

- [1] J. PALACIOS: *Análisis dimensional* (Madrid, 1956).
- [2] M. G. BECK: *Introduction à la théorie des quanta* (Coimbra, 1942).
- [3] W. FINKELBURG: *Atomic Physics* (New York, 1950).

PARTE SECONDA

SEZIONE TERZA: Varia.

The Solar Constant.

R. TOUSEY

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The Solar Constant is defined as the radiation density received from the sun at the earth, outside the atmosphere, and for the mean solar distance. It is usually measured in $\text{cal/cm}^2/\text{min}$, sometimes called Langleys after the astrophysicist S. P. LANGLEY, of the Smithsonian Institution, who pioneered in solar radiation measurements.

The solar constant cannot really be classed as a fundamental physical constant. In fact, strictly speaking, it is not a constant at all. Furthermore it refers to a property of an extremely large collection of particles, rather than to a single particle or elementary process. However, the solar constant, if we admit the use of this word, is certainly fundamental in relation to life on the earth. There can be little doubt that a permanent change in its value by more than a few percent in either direction would have a profound effect on the life of mankind, including us physicists, though the laws of physics would be unchanged.

Commencing early in this century, the solar constant has been the subject of a long series of investigations by the Smithsonian Institution and we may mention the names, C. G. ABBOT, F. E. FOWLE, L. B. ALDRICH and W. H. HOOVER. The basic measurements of the Smithsonian Institution have never been seriously questioned and to my knowledge this work stands to the present day as the best. A number of corrections, however, are involved in determining the best value given by their measurements. These have been the subject of much discussion for many years. The Smithsonian Institution has attempted both to measure the absolute value of the solar constant, and also to detect both short and long term variations in its value. It is not my intention to go into the question of variations in the solar constant, since this is a subject of much controversy, and since the variations reported by the Smithsonian are small, being less than 2%. What I wish to discuss is the absolute value of the solar constant.

The solar constant is, of course, given by the area under the curve of the spectral intensity of sunlight, outside the earth's atmosphere; once this curve is obtained, it is simple to integrate over the entire spectrum to obtain the solar constant. However, parts of the solar spectrum, especially the region below 2900 \AA , are so strongly attenuated by the atmosphere that they can only be observed from rockets. For other regions, particularly in the infrared, it is difficult to make exact corrections for attenuation due to the banded nature of the absorption by water vapor and carbon dioxide. These corrections, for the parts of the spectrum that could not be observed, have been the source of uncertainty in the exact value of the solar constant.

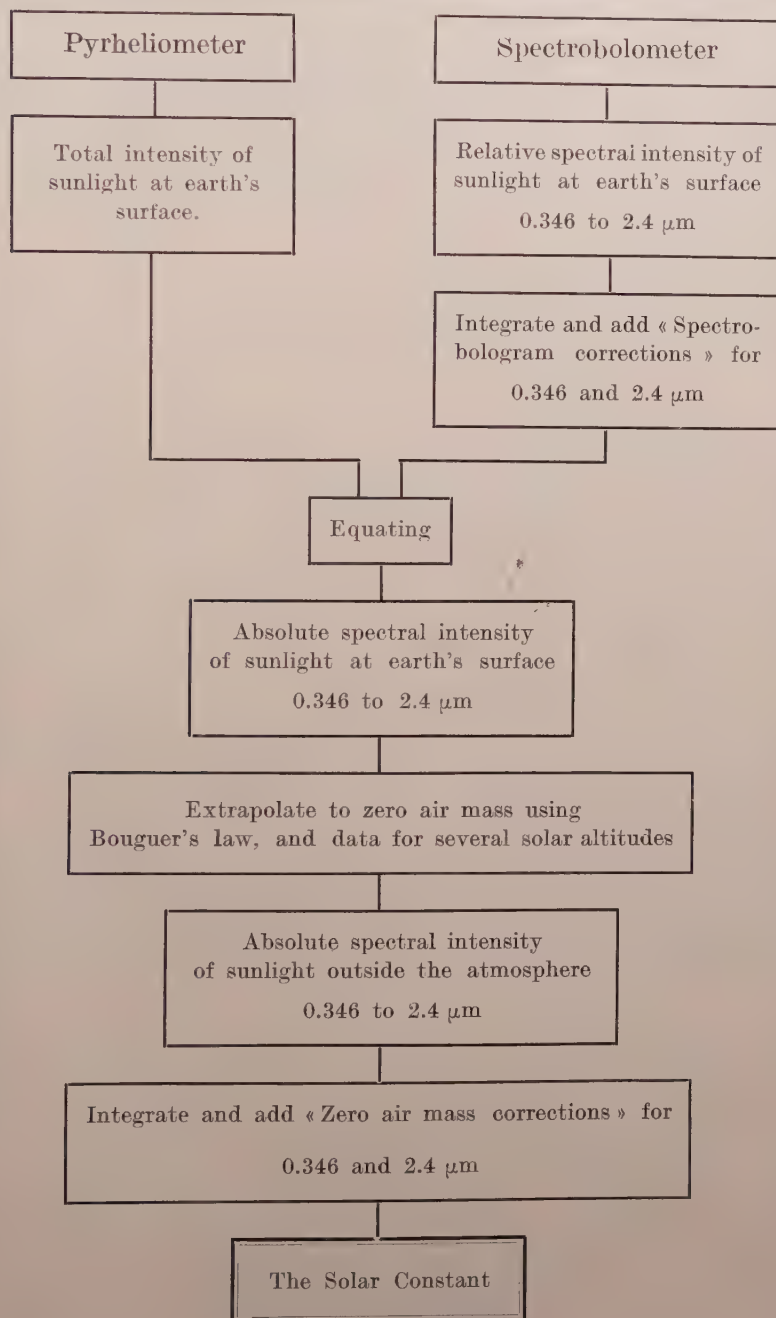
In 1953, the Naval Research Laboratory (NRL) found itself in a position to reevaluate the various corrections. This was possible, first, because the ultraviolet end of the solar spectrum had been remeasured, and extended to the wavelength range $2900\text{--}2200 \text{ \AA}$ by means of work performed from rockets; and second, because the Smithsonian Institution had just published a clarification of the various scales used by them in reporting the data. The work was done, principally, by F. S. JOHNSON [1].

In Table I is shown a block diagram to show how the Smithsonian approached the problem. Two measuring instruments are used. The one is a spectrophotometer. This simply measures the spectral intensity distribution of sunlight as it reaches the ground, and does so on a scale that is correct on a relative basis only. The other instrument is a pyrheliometer. This records the total solar intensity reaching the ground, without spectral resolution; the pyrheliometer gives the absolute value of the total energy, and is used to determine the absolute energy scale for the spectral intensity curve given by the spectrophotometer. The difficulty in carrying this out is connected with the fact that the spectral range covered by the spectrophotometer is limited to 0.346 to $2.4 \text{ }\mu\text{m}$, whereas the pyrheliometer is not so limited. Therefore, correction for the UV and IR ends of the solar spectrum reaching the earth must be determined before the pyrheliometer reading and the integrated area under the spectrograph can be compared. These corrections are called the spectrograph corrections. After making the corrections and normalizing we have the solar spectral intensity curve in the range 0.346 to $2.4 \text{ }\mu\text{m}$ on an absolute energy basis.

We proceed then starting with the spectral intensity curve in absolute units, as viewed through the atmosphere, over the wavelength range 0.346 to $2.4 \text{ }\mu\text{m}$. This is obtained in the way I have described for many values of the air mass, by making observations with the sun at different altitudes. Then an extrapolation is made to zero air mass, wavelength by wavelength, making use of Bouguer's exponential law of attenuation.

To obtain the solar constant, it is necessary to add to the area under this curve, the area under the ultraviolet end, beyond $0.346 \text{ }\mu\text{m}$ and the area under

TABLE I.

Procedure of the Smithsonian Institution to determine the solar constant.

the infrared end, beyond $2.4\text{ }\mu\text{m}$. These areas are the UV and IR zero air mass corrections, respectively.

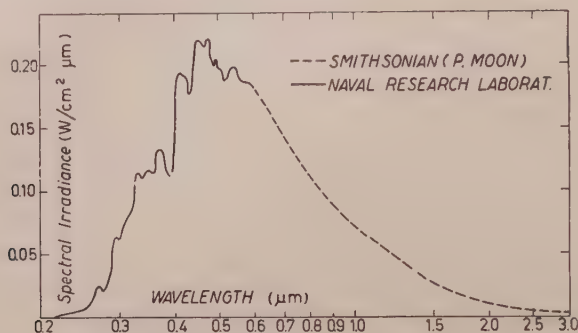


Fig. 1.

In all, then, there are four corrections to be determined. Before they can be properly calculated, it is necessary to have at hand the curve of spectral intensity distribution of sunlight, outside the atmosphere.

The spectral intensity distribution curve used by JOHNSON [2] for calculating the corrections is shown in Fig. 1. From 0.22 to $0.34\text{ }\mu\text{m}$ the data are those determined by direct observation from various NRL rocket flights. From 0.34 to $0.68\text{ }\mu\text{m}$ the data are those obtained in 1951 by DUNKELMAN and SCOLNIK [3] of our Laboratory from the top of Mount Lemmon in Arizona. The range from $0.6\text{ }\mu\text{m}$ as far into the infrared as one needs consider, is taken from a summary paper by MOON [4], based largely upon the work of the Smithsonian. From $1\text{ }\mu\text{m}$ out, the curve is a $6000\text{ }^\circ\text{K}$ gray body.

Bypassing further detail, I should like, now, to present the various revised numerical data. We start with the Smithsonian value of the Solar Constant. The confusion about the scale that has existed for many years was cleared up in 1952 by a paper by ALDRICH and HOOVER [5]. In Table II there is given the value in terms of the three different scales that have been used over the years.

TABLE II.

30 yr mean	
1.946 cal $\text{cm}^{-2}\text{ min}^{-1}$	Scale in actual use
1.981 cal $\text{cm}^{-2}\text{ min}^{-1}$	Scale of 1913
1.934 cal $\text{cm}^{-2}\text{ min}^{-1}$	Scale of 1932: the true scale
1.835 cal $\text{cm}^{-2}\text{ min}^{-1}$	Portion of solar constant 0.346 to $2.4\text{ }\mu\text{m}$

In their paper ALDRICH and HOOVER state that all the data have always been

given in terms of the scale in actual use; this is the scale which was maintained throughout the years. In this scale the best value of the solar constant is 1.946. The so-called scale of 1913 was 1.8% smaller, so that the value in this scale would be 1.981. The true value, however, is that of the 1932 scale and is 1.934.

Starting with this value, JOHNSON went over the correction procedure. It was necessary first to subtract out the Smithsonian zero air mass correction before applying new corrections. When this was done the Smithsonian value for the portion of the Solar Constant between 0.346 and 2.4 μm came out to be 1.835 in the true scale of 1932.

TABLE III.

NRL revision of solar constant

Smithsonian	NRL	
1.835	1.835	Smithsonian zero air mass energy 0.346 to 2.4 μm
—	0.006	Incr. due to rev. U. V. spectrobolometer corn' basis: Mt. Lemmon data
0.061	0.085	U. V. zero air mass correction ($\lambda < 0.346 \mu\text{m}$) basis: Mt. Lemmon and rocket data
0.038	0.076	I. R. zero air mass correction ($\lambda < 2.4 \mu\text{m}$) basis: 6000 °K black body sun (ADEL)
1.934	2.002	Final solar constant ($\text{cal cm}^{-2} \text{ min}^{-1}$)

In Table III we see the new values of the corrections recommended by the Naval Research Laboratory, together with the values of the corrections made by the Smithsonian for comparison. The value 1.835 included both the ultraviolet and infrared spectrobologram corrections, as made by the Smithsonian. The infrared spectrobologram correction appeared not to need revision. The recalculation of the UV spectrobologram, making use of our revised solar curve determined from Mount Lemmon, indicated an increase of 0.006. A much greater change is required by the new value of the UV zero air mass correction. The Smithsonian value was 0.061 whereas, our value, based on the Arizona and rocket results is 0.085. The largest change, however, is due to the infrared zero air mass correction. The Smithsonian value of 0.038 was based on an improper extrapolation to zero air mass of infrared atmospheric transmission. What they did was to determine the correction by direct spectrobolometric measurement of the solar spectrum out to 10 μm , for different amounts of water vapor in the air path, ranging from 2.5 to 5.4 cm. Then the correction was extrapolated more or less linearly, to zero water vapor. From calculations such as have been made by YATES [6] of atmospheric transmission in the infrared as a function of water vapor content it can be shown

that this extrapolation results in much too small a value of the correction. The reason is that very small amounts of water vapor absorb very strongly. The correction curve rises sharply some where below 1 cm of water vapor. Instead of attempting to compute a correction from a crude extrapolation of the attenuation, JOHNSON based the correction on the solar curve outside the earth's atmosphere. The curve from $2.4 \mu\text{m}$ to at least $14 \mu\text{m}$ has been shown by ADEL [7] and by PEYTUREAU [8] to have the shape of a 6000°K black body distribution. The resulting value of the correction is 0.076, just twice the value of the correction used by the Smithsonian.

After application of these corrections, the final result for the solar constant is $2.002 \text{ cal/cm}^2 \text{ min}$. We prefer to call it 2.00 since we feel that the probable error may be of the order of $\pm 2\%$.

I feel that new work on the solar constant is very much in order, but it will not be easy to improve on the accuracy attained by the Smithsonian. Attempts to make measurements directly from rockets have been made but not yet with completely satisfactory results. The values obtained were of the order of 2.0 however. Measurements from the ground could now be made with increased accuracy due to the present day availability of many new radiation measuring techniques. To do this, however, will require a long series of painstaking measurements, preferably, from two independent stations located at widely separated points on the earth.

REFERENCES

- [1] F. S. JOHNSON: *Journ. of Meteorology*, **11**, no. 6, 431 (1954).
- [2] F. S. JOHNSON, J. D. PURCELL, R. TOUSEY and N. WILSON: *Rocket exploration of the upper atmosphere* (London, 1954), p. 279.
- [3] L. DUNKELMAN and R. SCOLNIK: *Journ. Opt. Soc. Am.*, **42**, 876 (1952) (Abstract).
L. DUNKELMAN and R. SCOLNIK: to be published in *Journ. Opt. Soc. Am.*
- [4] P. MOON: *Journ. Franklin Inst.*, **230**, 583 (1940).
- [5] L. B. ALDRICH and W. H. HOOVER: *Science*, **116**, 3 (12 December, 1952).
- [6] H. YATES: *Washington, Naval Res. Lab.* (Rep. 3858), (1951).
- [7] A. ADEL: *Astrophys. Journ.*, **89**, 1 (1939); *Journ. Opt. Soc. Am.*, **37**, 769 (1947).
- [8] R. PEYTURAUX: *Ann. Astrophys.*, **15**, 302 (1952).

Sur les radiations monochromatiques envisagées pour une nouvelle définition de l'unité de longueur.

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1. - Une définition du mètre par une longueur d'onde qui soit une constante naturelle.

En 1829, le physicien français J. BABINET, contemporain d'AVOGADRO, faisait remarquer que la longueur des ondulations lumineuses dans le vide pourrait constituer un étalon de longueur constant et reproductible. On voudrait aujourd'hui trouver une longueur d'onde atomique dans le vide qui fût non seulement un étalon constant et reproductible, comme l'a été la raie rouge du cadmium, mais encore une constante naturelle. La longueur d'onde de la raie rouge du cadmium est en effet reproductible à $\pm 2 \cdot 10^{-8}$ près en valeur relative à la condition que la lampe soit conforme à des spécifications édictées par la Conférence Générale des Poids et Mesures. Pour remplacer le mètre étalon en platine iridié du Pavillon de Breteuil, le Comité International des Poids et Mesures a reçu mission de soumettre en 1960 à la Conférence Générale le projet d'une nouvelle définition; jusqu'ici, il n'a pu que sanctionner la Résolution suivante, adoptée par le Comité Consultatif constitué spécialement, sans pouvoir fixer son choix sur la radiation qui réponde le mieux aux qualités désirées:

« Le Comité Consultatif considère que le mètre devrait être défini, lorsque le moment sera venu, par la longueur d'onde d'une radiation lumineuse se propageant dans le vide, le radiateur et l'observateur étant en repos relatif.

« Cette radiation serait spécifiée par deux termes spectraux d'un atome dont le spectre soit dépourvu de structure hyperfine, et qui ne soit soumis à aucune influence perturbatrice ».

Ce projet ambitieux conférerait au futur étalon de longueur la qualité de constante naturelle, calculable à partir de la vitesse de la lumière, de la constante de Planck et de l'énergie des termes spectraux; cette énergie est d'ailleurs calculable, en principe, à partir des constantes fondamentales.

Mais d'autre part, on ne peut obliger un atome à émettre une radiation sans le soumettre à une perturbation; dans la lampe qu'il faudra bien réaliser pour mesurer une longueur avec un tel étalon, les atomes seront nombreux, se perturberont mutuellement, et ne seront pas en repos par rapport à l'appareil d'observation. Dans quelle mesure s'est-on approché d'un idéal irréalisable, telle est la question qui sera envisagée ici, d'après les études expérimentales que nous poursuivons actuellement au Bureau International des Poids et Mesures.

2. - Rappels théoriques.

Voyons d'abord ce que nous apprend la théorie, en nous bornant au seul cas des radiations sans structure hyperfine, choisies parmi les plus fines, et produites dans une lampe où les perturbations sont faibles.

On sait que la théorie quantique du rayonnement prévoit qu'une radiation atomique, même dans des conditions idéales, n'est pas strictement monochromatique, mais occupe un petit domaine spectral, avec une répartition d'intensité symétrique autour de la fréquence moyenne, et une certaine largeur à mi-intensité, largeur dite naturelle, petite devant les élargissements dûs à d'autres causes; sa valeur est de l'ordre de 10^{-4} Å.

L'effet Doppler-Fizeau produit généralement l'élargissement principal, trente à cent fois plus important que la largeur naturelle. Mais le profil spectral élargi par cet effet conserve le même axe de symétrie, axe qui définit encore la même longueur d'onde sans ambiguïté, avec une précision moins bonne, à la condition que les atomes soient en état d'agitation purement thermique, sans mouvement d'ensemble dirigé.

L'élargissement par résonance est dû à l'interaction quantique entre atomes semblables; il ne change pas l'axe de symétrie du profil spectral.

L'autoabsorption, généralement plus prononcée dans la partie centrale du profil spectral d'une radiation, peut élargir fortement ce profil, et même lui donner l'apparence d'un doublet lorsque la raie est complètement renversée. Une raie émise dans la région centrale de la lampe est partiellement réabsorbée par les atomes marginaux moins perturbés. Les raies de résonance dont le terme inférieur est l'état normal, et celles dont le terme inférieur est métastable, sont les plus facilement renversées. Une raie renversée de profil spectral symétrique pourrait encore définir une longueur d'onde par son axe de symétrie, mais d'une façon fort peu satisfaisante.

L'effet Zeeman est en général négligeable, et son action reste symétrique.

Enfin, le plus redouté est l'effet Stark, provoqué par les champs électriques appliqués à la lampe, par le champ des ions, des électrons, et des atomes neutres voisins de l'atome émetteur, car il élargit le profil spectral d'une façon dissymétrique, en même temps qu'il déplace la longueur d'onde du maximum. Nous rangeons sous la même désignation ce que l'on a appelé l'effet de pression. Ces effets sont de plus en plus intenses lorsque le nombre quantique principal du terme supérieur s'élève, c'est-à-dire lorsque l'orbite électronique s'agrandit.

On peut donc chercher à produire une radiation presque naturelle en excitant faiblement un gaz à basse pression, et en choisissant une raie dont le terme supérieur ne soit pas trop élevé afin d'éviter les conditions propices à l'effet Stark. De plus, on devra éviter aussi les causes d'élargissement symétrique, non seulement pour se rapprocher du profil naturel, mais aussi pour que la longueur d'onde moyenne du profil spectral symétrique soit définie avec plus de précision, et encore pour qu'une légère dissymétrie résiduelle soit plus aisément décelable.

Voyons maintenant quelques-unes des études expérimentales que nous avons entreprises en vue de mieux connaître les caractéristiques des radiations produites dans quelques lampes réelles.

3. - Lampes étudiées.

Les radiations étudiées ont été produites par l'une des quatre lampes suivantes.

Un tube sans électrode contenant 3 mg de ^{198}Hg et de l'argon sous une pression de 0.5 à 1 mm de mercure, que l'on excite dans le champ de haute fréquence d'un oscillateur à 300 MHz environ; il est entouré d'une chemise de liquide en circulation dont on peut régler la température entre -2 et $+50$ °C. Cette lampe a toujours été observée en travers. Elle a été offerte par le National Research Council d'Ottawa.

Une lampe à cathode chaude de Engelhard contenant du ^{86}Kr . Cette lampe est immergée dans un bain d'azote liquide que l'on refroidit par pompage jusqu'au point triple de l'azote 63 °K. Le courant de décharge est 20 mA, et la densité de courant environ 7 mA/mm². On l'observe généralement en bout du capillaire. Quelques expériences ont été faites avec observation en travers.

Un tube sans électrode contenant du ^{86}Kr et refroidi dans les mêmes conditions. Il a été observé en bout et en travers.

Un tube sans électrode contenant 3 mg de ^{113}Cd et de l'argon à une pression de 3 mm de mercure, excité en haute fréquence dans un four à $230 \div 280$ °C.

4. — Visibilité des interférences à deux ondes.

Comme l'a montré MICHELSON, il existe une relation entre le profil spectral d'une radiation et la variation de la visibilité des interférences dans un interféromètre de Michelson lorsqu'on augmente la différence de marche. Rappelons que, I_{\max} et I_{\min} étant l'éclairement du champ de franges à un maximum et à un minimum, la visibilité est définie par $V = (I_{\max} - I_{\min}) / (I_{\max} + I_{\min})$. Si la visibilité ne décroît pas régulièrement, il est certain que le profil de la raie n'est pas simple et symétrique. Nous avons constaté par cette méthode que la raie verte du ^{198}Hg , la lampe étant à 20°C , et la raie verte intense 5570 \AA du ^{86}Kr ne sont pas normales; la visibilité passe par un minimum, puis augmente à différence de marche plus grande; la deuxième de ces raies a permis de voir des interférences à la différence de marche de 90 cm. En revanche, la raie infrarouge du krypton, 9856 \AA semble se comporter normalement; les interférences ont été photographiées, avec une visibilité décroissante, aux différences de marche 50, 75, 85, 95, et 100 cm.

Une autre méthode d'étude consiste à maintenir invariable la différence de marche, et à mesurer la visibilité pendant que l'on change les conditions d'excitation de la lampe. Ainsi, nous avons constaté que la fréquence du champ

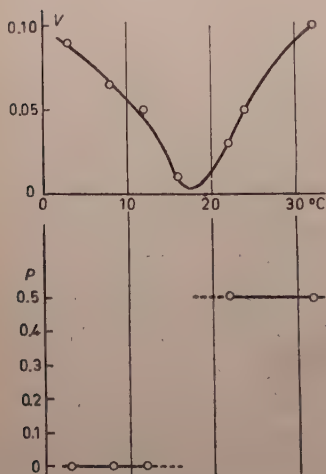


Fig. 1. — Etude de la raie $0.54607529\text{ }\mu\text{m}$ du ^{198}Hg à l'interféromètre de Michelson; différence de marche 400 mm. V visibilité en fonction de la température de la lampe t . p excédent fractionnaire de l'ordre d'interférence en fonction de t .

oscillant et la puissance dépensée dans l'oscillateur associé à la lampe à mercure 198, ou l'intensité du courant dans la lampe à krypton de Engelhard, avaient fort peu d'effet sur la visibilité, sauf dans le cas de la raie verte du mercure lorsqu'elle est renversée.

La température de la lampe est au contraire un facteur important; c'est elle qui règle la pression de l'élément émetteur par la variation de sa tension de vapeur. Les deux raies du ^{198}Hg de longueur d'onde 5461 et 4356 \AA , surtout la première, se renversent progressivement lorsque la température monte de -2 à $+32^\circ\text{C}$; en effet la visibilité décroît, s'annule, puis les franges réapparaissent, mais une frange claire a pris la place d'une frange sombre, et inversement; chacune de ces raies se comporte donc comme un doublet (Fig. 1). Pour la raie verte, on a répété ces observations à plusieurs différences de marche, entre 40 et 60 cm; par extrapolation, on trouve que l'écartement du doublet que constitue la raie renversée tend

vers zéro pour une température de la lampe voisine de 0°C . Au contraire, la raie jaune 5791 \AA garde à peu près la même visibilité, avec une décroissance de 10 à 15 pour cent lorsque la température de la lampe atteint 32°C (Fig. 2).

L'étude des raies du krypton de la lampe Engelhard vue en bout par la même méthode a montré, entre 63°K et 83°K , que la visibilité des interférences des raies intenses 5871 \AA et 5570 \AA est toujours anormalement faible, et que l'élargissement de la raie verte 5570 \AA ne semble pas avoir pour cause un renversement simple comme le laissait penser l'observation faite à différence de marche croissante. Les raies 5650 \AA et 6056 \AA , surtout la seconde, sont celles qui présentent la meilleure visibilité de toutes les raies étudiées dans le spectre visible; cette visibilité diminue de moitié environ, à la différence de marche de 40 cm, lorsque la température monte de 63°K à 83°K .

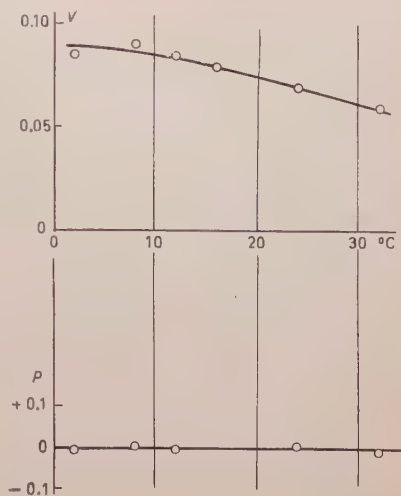


Fig. 2. Etude de la raie $0.57906624 \mu\text{m}$ du ^{198}Hg à l'interféromètre de Michelson; différence de marche 400 μm . V visibilité en fonction de la température de la lampe, t . p excédent fractionnaire de l'ordre d'interférence en fonction de t .

5. - Étude du profil spectral avec un étalon Perot-Fabry.

Un étalon Perot-Fabry de 62.5 mm en invar, muni de deux miroirs à 7 couches diélectriques, a été enfermé dans une enceinte étanche où l'on peut modifier l'indice de réfraction de l'air par variation de la pression. Les anneaux à l'infini sont focalisés sur un écran opaque percé d'un trou axial, qui laisse passer la lumière vers un photomultiplicateur suivi d'un enregistreur à plume. Pendant la variation de pression, on enregistre ainsi le profil spectral d'une radiation, dont la largeur est par exemple 20 mK ($1 \text{ mK} = 10^{-3} \text{ cm}^{-1}$), avec cet appareillage dont la bande passante est 1 à 3 mK pour la région spectrale $5400 \div 6400 \text{ \AA}$. Cette région a été choisie pour l'ajustage des couches diélectriques des miroirs qui ont été préparées au Laboratoire Aimé Cotton à Bellevue.

Le profil spectral de la raie verte 5461 \AA du ^{198}Hg , le tube étant refroidi au voisinage de 0°C , a une largeur à mi-hauteur de 20.5 mK; la largeur Doppler théorique est 15.5 mK. Il serait important de savoir si l'accroissement de largeur de 30 pour cent constaté provient d'une température

plus élevée de la vapeur de mercure dans la région lumineuse, d'un effet de pression, ou d'un effet Stark dû au champ de haute fréquence. Une analyse encore plus fine du profil pendant que l'on impose des changements systématiques aux conditions d'excitation fournira peut-être une réponse à ces questions.

Lorsque la lampe est à 20 °C, le profil de cette raie verte paraît élargi; l'examen quantitatif de la courbe enregistrée révèle que le sommet est moins

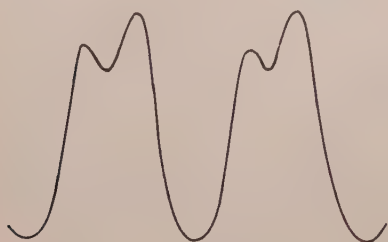


Fig. 3. — Étude de la raie 0.546 075 29 μm du ^{198}Hg à l'étalon Perot-Fabry. Profil spectral lorsque la lampe est à la température 40 °C.

aigu; dans ces conditions, la variation de la visibilité à l'interféromètre de Michelson a montré que cette raie verte se comporte alors comme un doublet dont l'écartement serait 12 mK environ.

La lampe étant à 40 °C, le profil est franchement renversé (Fig. 3); de plus, les deux maxima d'intensité qui encadrent le minimum central ne sont pas symétriques; par rapport à la raie d'absorption, moins perturbée, la raie d'émission est décalée vers les grandes longueurs d'onde. On a là la preuve que la longueur d'onde de cette raie

augmente lorsque la pression du mercure augmente.

Des phénomènes analogues, mais avec un déplacement vers les courtes longueurs d'onde, ont été observés, avec des miroirs aluminés, pour la raie 4358 Å du ^{198}Hg (Fig. 4).

Au bas d'un des flancs du profil enregistré de la raie verte 5461 Å, une légère dissymétrie a été remarquée; on s'est aperçu qu'elle s'expliquait quantitativement par la superposition des deux composantes hyperfines principales du ^{199}Hg , qui se trouve mélangé au ^{198}Hg de notre tube dans la proportion de 1.5 pour cent. Ceci illustre la sensibilité de cette méthode d'analyse.

Les raies jaunes 5769 et 5791 Å, entre 0 et 20 °C, gardent le même profil

et la même largeur de 20 mK environ, largeur qui croît jusqu'à 24 mK à 40 °C. L'essai d'une lampe à électrodes internes refroidie à 20 °C, mais contenant

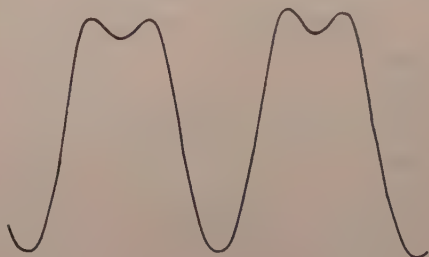


Fig. 4. — Étude de la raie 0.435 833 72 μm du ^{198}Hg à l'étalon Perot-Fabry. Profil spectral lorsque la lampe est à la température 40 °C.

de l'argon à la pression de 10 mm de mercure, au cours duquel on a observé une largeur de 29 à 30 mK pour ces raies jaunes, indique que la pression de l'argon produit un élargissement.

Avec la lampe à krypton de Engelhard refroidie à 63 °K et observée en bout, la raie verte intense 5570 Å a une largeur de 25 mK; au cours du refroidissement, son profil et son intensité varient d'une façon complexe; mais, observée en travers, sa largeur est 14 mK; l'élargissement dans l'observation en bout est donc, semble-t-il, la conséquence d'une autoabsorption accompagnée de changements de forme et de déplacements de la raie d'émission; l'effet de résonance que l'on croyait responsable jusqu'ici ne semble pas confirmé.

La raie la plus fine, comme on l'avait déjà constaté à l'interféromètre de Michelson, est 6056 Å, sa largeur, que l'observation soit faite en bout ou en travers, est 13 mK (Fig. 5).

La largeur théorique due à l'effet Doppler seul serait 10 mK. Il est vraisemblable que les perturbations qui portent de 10 à 13 mK la largeur de cette radiation sont moins graves que les perturbations qui élargissent les raies du mercure de 15.5 à 20 mK; en effet, plus un profil est étroit, plus il est élargi facilement. De plus, l'égalité des largeurs dans l'observation en bout et en travers tend à prouver que l'autoabsorption est négligeable. La raie 5649 Å a des qualités semblables.

La lampe sans électrode à krypton a donné des résultats analogues, avec des largeurs légèrement supérieures, peut-être parce que son refroidissement a été moins efficace, peut-être parce que l'excitation en haute fréquence perturbe davantage que la décharge à cathode chaude.

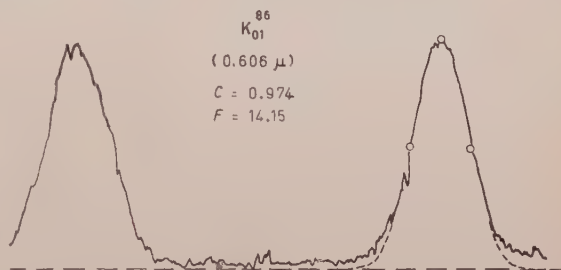


Fig. 5. — Profil spectral de la raie 0.605 612 53 μm du ^{86}Kr , la lampe étant à 63 °K. Les points ont été calculés et représentent la courbe théorique de Gauss ayant même largeur que le profil expérimental en trait continu.

6. — Comparaisons précises de longueur d'onde.

Les méthodes classiques de comparaison de longueur d'onde, telles qu'elles ont été pratiquées par PÉRARD à l'interféromètre de Michelson, et par de nombreux autres expérimentateurs avec des étalons Perot-Fabry, exigent, pour que soit garantie une précision suffisamment élevée de l'ordre de 10^{-8} , des précautions minutieuses et des mesures nombreuses. Mais lorsque l'on dispose

de deux sources de lumière produisant des radiations ayant à peu près la même longueur d'onde, l'une peut rester invariable et fournir un repère pour l'évaluation des variations de l'autre. Ainsi, en entremêlant alternativement la raie rouge du cadmium de deux lampes sur le même ensemble enregistreur de profil spectral, avons nous pu comparer l'émission de la lampe de Michelson conforme aux spécifications internationales, et l'émission du tube sans électrodes à ^{114}Cd , lorsque ce tube est porté successivement à 230 °C, 250 et 270 °C (Fig. 6).

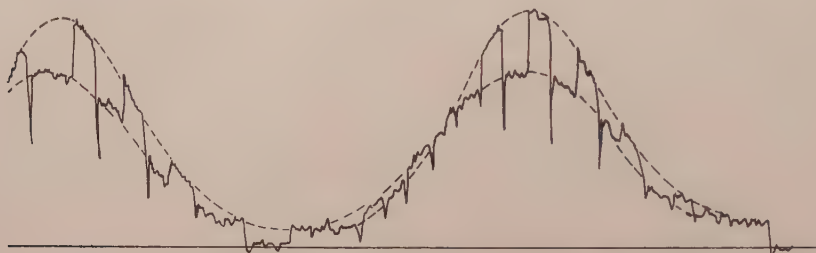


Fig. 6. — Profils spectraux entremêlés de la raie rouge du ^{114}Cd (courbe inférieure) et de la raie rouge du cadmium ordinaire de la lampe Michelson (courbe supérieure).

La longueur d'onde de la raie rouge du ^{114}Cd émise par cette lampe diminue légèrement, de 6438, 4688 à 6438, 4685, pendant cette élévation de la température. On sait d'autre part que la présence d'argon, comme dans le cas du ^{198}Hg , déplace cette longueur d'onde de quelques dix-millièmes d'angström vers les grandes longueurs d'onde. Sa largeur observée est 31 à 33 mK, la largeur Doppler théorique étant 23 mK. Ce changement de la longueur d'onde à température variable ne nous a pas surpris, car des expériences antérieures, avec un tube sans électrode contenant du cadmium ordinaire, avaient décelé une diminution du même ordre de la longueur d'onde du maximum lorsqu'on élevait la température de 270 à 290 °C.

La largeur observée de la même radiation rouge de la lampe de Michelson est 35 mK, mais on sait que les isotopes pairs du cadmium émettent des longueurs d'onde différentes et que les isotopes impairs ont une structure hyperfine, ce qui explique que la largeur soit plus grande.

La raie verte 5086 du ^{114}Cd a été trouvée fortement renversée, bien que le tube ait toujours été observé en travers, et cela même à la température relativement basse de 230 °C.

7. — Conclusion.

Les expériences récentes que nous venons de mentionner constituent un premier travail d'exploration destiné à mettre à l'épreuve quelques méthodes d'étude, en vue de choisir une radiation peu sensible aux perturbations inévi-

tables, et de rechercher des méthodes d'excitation peu perturbatrices. Parallèlement à ces études faites au Bureau International, quelques autres laboratoires travaillent vers le même but. Il apparaît que, jusqu'ici, jamais on n'a réussi à produire une radiation dont la largeur soit la largeur Doppler théorique à la température de l'enceinte où est placée la lampe. Les causes de cet élargissement supplémentaire devraient être trouvées pour que l'on sache comment les combattre. Des perfectionnements aux méthodes envisagées ici apporteront peut-être une solution à ce problème. Si l'on y parvient, la future définition de l'unité de longueur, que la Conférence Générale des Poids et Mesures a l'intention d'édicter en 1960, pourra garantir à la science la précision et l'invariabilité de l'étalon de longueur qui sont désirables pour exprimer la mesure des grandeurs où une longueur intervient, et en particulier, pour exprimer la valeur des constantes fondamentales du monde physique.

La détermination optimum d'une constante physique par le relevé de lois expérimentales.

P. VERNOTTE

Ministère de l'Air, Paris

Soit une grandeur physique G intervenant dans une loi expérimentale y de la variable x , de forme connue, comportant en outre P paramètres λ_j . La méthode traditionnelle consiste à mesurer y pour $P+1$ valeurs de x , et à résoudre le système des $P+1$ équations obtenues, qui donnera accessoirement les P paramètres λ_j , et avant tout la grandeur G .

Il est de bonne règle de recommencer N fois l'opération pour préciser mieux que par toute autre méthode l'incertitude δG frappant G , et en réduire l'influence.

Il arrive que la connaissance de G ne puisse être que très indirecte, résultant de la connaissance, à demander à l'expérience, d'autres grandeurs physiques Γ_k qui seraient déterminées, au mieux, comme il vient d'être dit (par exemple, parallaxe solaire).

Nous avons personnellement beaucoup insisté sur ce fait qu'une grandeur G ne devait pas être ainsi déterminée au moyen du nombre de données juste nécessaire, mais qu'il y avait lieu d'étudier méthodiquement un phénomène y pour déduire G des propriétés de la loi y . (Par exemple, les caractéristiques d'un système optique seraient déduites de l'étude de la position de l'image en fonction de la position de l'objet). A dire vrai, cette procédure avait été parfois employée déjà, mais, d'une part, ce n'était pas systématique, et surtout on suivait une procédure qui nous semble peu judicieuse. Car si, à partir de mesures nombreuses, on déterminait bien la loi y par la méthode des moindres carrés qui donne au mieux la loi y elle-même, ce n'était pas elle que l'on avait besoin de connaître au mieux: on veut G , on n'a que faire de y , la connaissance au mieux de la loi y dans son ensemble n'est pas ce qui conditionne la meilleure connaissance de G .

Nous appliquons une méthode complètement différente.

La loi y comportant P paramètres, nous partageons l'intervalle expérimental en P sous-intervalles, le long desquels nous identifions la valeur moyenne du phénomène mesuré et de sa représentation théorique y . Le problème essentiel est de déterminer les bornes des sous-intervalles. Nous y arrivons en écrivant que les incertitudes ε_i de chaque mesure ont une influence minimum sur l'incertitude δG , calculée à partir des ε_i par les règles du calcul différentiel. Ce minimum est normalement réalisé quand les coefficients de tous les ε_i dans δG sont égaux en valeur absolue (lorsque les abscisses sont équidistantes), ce qui détermine les bornes cherchées.

Cette partition de l'intervalle expérimental a une influence considérable sur δG ; elle dépend essentiellement de la manière dont G (qui peut être l'un des paramètres) est liée aux paramètres de la loi, ce qui explique que les résultats soient très différents de ceux de la méthode des moindres carrés, qui n'offre aucune nuance. Si G , par exemple, est le coefficient du terme du second degré dans une loi parabolique, on trouve que notre méthode entraîne une insécurité presque deux fois plus faible que la méthode des moindres carrés. Il faut bien rappeler ce fait fondamental qu'une procédure doit être toujours strictement adaptée au but recherché.

Une série de relevés joue exactement le même rôle que le groupe des P ou $P+1$ mesures de la procédure traditionnelle, et constitue, au même titre, une expérience. On fera N séries de relevés comme on faisait N groupes de P ou $P+1$ mesures. Une série de relevés conduisant à une bien autre sécurité qu'un tel groupe de mesures, il s'ensuit que la précision de la détermination sera très augmentée.

Dans le cas où G dépend d'autres grandeurs Γ_k , chaque grandeur Γ_k sera déterminée par relevé expérimental méthodique, les partitions des intervalles expérimentaux correspondants étant déterminées par la condition que les incertitudes expérimentales, lors des mesures, entraînent finalement un δG minimum. On calcule δG par les règles du calcul différentiel, à partir des ε_i originaux, en passant par l'intermédiaire des $\delta \Gamma_k$.

En résumé, on tirera la connaissance de la grandeur G cherchée, de l'étude de diverses lois expérimentales, étude conduite non en vue de la connaissance optimum de ces lois, mais selon la procédure spéciale qui rendra la connaissance de G aussi peu sensible que possible aux imprécisions des mesures originales.

PARTE TERZA

Sunti delle comunicazioni presentate al Congresso della Società.

A. ALBERIGI QUARANTA, F. LEPRI, M. PUGLISI e I. F. QUERCIA (*Roma*). — **Descrizione dell'impianto a radio frequenza modulata realizzato per il sincrotrone nazionale.**

Nell'attuale progetto per il Sincrotrone Nazionale da 1000 MeV, gli elettroni vengono iniettati entro la ciambella con energia cinetica di 2 MeV, e vengono accelerati sino all'energia finale mediante due cavità risonanti a radio frequenza. La prima cavità ha il compito di accelerare gli elettroni dall'energia di iniezione sino ad un'energia di circa 7 MeV. Durante questa prima parte del ciclo di accelerazione, la frequenza di rivoluzione degli elettroni nella ciambella varia di circa il 2.1%; la frequenza della cavità, e l'impianto a radio frequenza che la alimenta, deve naturalmente seguire tale variazione di frequenza. Pertanto esso è un impianto a Radio Frequenza Modulata in Frequenza (RFMF). La seconda cavità ha il compito di accelerare gli elettroni da circa 7 MeV all'energia finale. Nell'ultima parte del ciclo di accelerazione gli elettroni perdono una notevole quantità di energia per radiazione. Tale energia, insieme a quella necessaria all'accelerazione, deve essere rifornita dal secondo impianto a Radio Frequenza Fissa (RFF), il quale quindi è di potenza notevole. L'impianto RFMF è stato progettato e realizzato presso la Sezione Acceleratore dell'Istituto Nazionale di Fisica Nucleare. Esso è attualmente in fase di messa a punto. Qui appresso ne sono riassunte le principali caratteristiche: — cavità risonante tipo rientrante inserita direttamente sul circuito di placca della valvola finale; — valvola finale da 10 kW montata griglia a massa; — gruppo eccitatore della valvola finale costituito da: a) oscillatore pilota modulato in frequenza con tubo a reattanza, b) catena di triplicazione della frequenza e di amplificazione di potenza sino ad 1 kW, — frequenza pari alla IV armonica della frequenza di rivoluzione degli elettroni; — variazione massima possibile della frequenza da 42.6 a 43.7 MHz pari al 2.5%; — tolleranza sul valore istantaneo della frequenza rispetto al valore teorico: $\pm 0.1\%$; — massima tensione di picco a Radio Frequenza fornita dalla cavità: 7000 V; — programma della modulazione di frequenza e della modulazione di ampiezza controllato elettronicamente, ed asservito al valore istantaneo del campo magnetico nel traferro del sincrotrone; — sistema elettronico automatico di correzione degli errori nel circuito di programmazione; — possibilità di comandare e controllare il funzionamento dell'impianto a distanza.

F. ANDERSON, D. KEEFE, A. KERNAN and J. LOSTY (*Dublin*). — **Interactions in flight of positive heavy mesons in emulsion.**

This work has been carried out in a stack (Stack K2) of stripped emulsions exposed to the K^+ beam at the Bevatron. The method of « on track » scanning was used and about 70 metres of K^+ -meson track have been scrutinized in an unbiased manner. Interactions and scatterings both elastic and inelastic have been observed for K-particles with all kinetic energies between 0 and 140 MeV. Distributions in the elastic (i.e. potential) scattering angles of K-particles by emulsion nuclei have been constructed at various energies and are believed to be unbiased for angles greater than 15° . The inelastic events have been studied in detail and it is shown how these may throw some light on the K^+ -nucleon interaction. The experimental difficulties implicit in the distinction between elastic events and those of small inelasticity are discussed. In contrast to the results published by the Göttingen group, only a small number of K^+ -hydrogen collisions has been observed.

G. L. BACCHELLA, M. DI CORATO, R. LEVI SETTI, L. SCARSI (*Milano*), A. BERTHELOT, O. GOUSSU (*Saclay*), M. RENÉ, D. REVEL, G. VANDERHAEGHE (*Bruxelles*) e G. TOMASINI (*Genova*). — **Misura dell'energia di disintegrazione del mesone τ e determinazione della relazione percorso-energia nell'intervallo $0.27 < \beta < 0.67$.**

L'energia di disintegrazione del mesone τ è stata misurata su una parte del K_1 Stack esposto al fascio dei K^+ del Bevatrone di Berkeley. Sono stati misurati gli angoli nello spazio fra i tre secondari ed il loro percorso nell'emulsione. Imponendo la condizione di complanarità ed adottando un valore di Q arbitrario, sono state calcolate le energie dei tre secondari ed è stata così ottenuta una relazione percorso-energia, che è funzione del valore di Q adottato. La particolare curva percorso-energia, che passa per il punto corrispondente al percorso, misurato nelle stesse lastre, dei μ da $\pi \rightarrow \mu + \nu$, definisce il valore di Q compatibile con le nostre misure; esso è: (74.9 ± 0.4) MeV. La relazione R - E trovata può essere messa nella forma:

$$\log_{10} \left(\frac{E}{mc^2} 10^3 \right) = 1.649 + 0.566 \log_{10} R_{mm} + 0.010 (\log_{10} R_{mm})^2.$$

F. BACHELET e A. M. CONFORTO (*Roma*). — **Aumento straordinario dell'intensità dei raggi cosmici associato con l'eruzione solare del 23 Febbraio 1956.**

Il 23 Febbraio 1956 alle 3.45 T.U. la Stazione Variazioni Intensità Raggi Cosmici (SVIRCO) esistente presso l'Istituto di Fisica dell'Università di Roma ha registrato un aumento eccezionale del numero di particelle ionizzanti in arrivo al livello del mare. L'apparecchio rivelatore (*) consta di 12 telescopi di contatori di

(*) F. BACHELET e A. M. CONFORTO: *Nuovo Cimento*, **12**, 951 (1954).

Geiger e Müller in coincidenza tripla, dei quali 4 diretti secondo la verticale, 4 inclinati di 30° rispetto alla verticale verso Nord nel piano meridiano geografico e 4 inclinati di 30° verso Sud nello stesso piano. L'aumento ha avuto inizio fra le 03 30 e le 03 45 T.U. e l'intensità ha raggiunto il massimo ($\sim 300\%$ del valore normale) fra le 03 45 e le 04 00 T.U., per poi ritornare al valore normale nel giro di circa 2 ore. L'evento va messo in relazione con l'eruzione solare, la cui osservazione dagli Osservatori Astronomici di Tokyo e di Kodaikanal è iniziata alle 3.34 T.U., ed è dello stesso tipo di 4 aumenti eccezionali d'intensità seguiti a eruzioni solari e osservati da più stazioni durante il decorso ciclo di attività solare, ma presenta rispetto ad essi caratteristiche di particolare violenza. Esso è il primo osservato nel nuovo ciclo undecennale. L'entità dell'aumento registrato contemporaneamente in tutto il mondo sulle varie componenti dei raggi cosmici e alle varie latitudini e longitudini è compatibile con l'ipotesi che si tratti di particelle di bassa energia emesse dal sole al momento del brillamento e incurvate dal campo magnetico terrestre così da pervenire anche nella parte oscura dell'emisfero terrestre.

M. BALDO-CEOLIN, M. CRESTI, N. DALLAPORTA, M. GRILLI, L. GUERRIERO, M. MERLIN, G. A. SALANDIN and G. ZAGO (*Padova*). — **Results on K^+ Interactions.**

K^+ interactions have been observed in two different stacks exposed to the K^+ beam of the Bevatron. The momenta of the particles focussed in the emulsion lie between 340 and 460 MeV/c. The scanning was by following the tracks. Only interactions due to primary K's with energy greater than 40 MeV have been considered. The total path length of track observed up until now is: 50.7 m of track with energy from 40 to 90 MeV, 41.7 m of track with energy from 90 to 160 MeV. A total of 224 events has been observed, of which 32 are decays in flight, 175 interactions with a secondary K emerging (of these 9τ), charge exchanges and 11 stops. Scattering were only accepted as such when the projection of the angle between primary and secondary K on the plane of the emulsion was greater than 12° . The interactions have been divided into elastic and inelastic ones according to criteria which are discussed at length. Moreover the events have been grouped into two different energy groups: 40–90 MeV and 90–160 MeV. We thus obtain 113 elastic events, (91 in the low energy and 22 in the high energy range) and 50 inelastic events (23 in the low and 27 in the high energy range). The mean free path for inelastic scattering which we obtain is: 1.4 ± 0.23 m for the energy interval 40 to 90 MeV, 1.3 ± 0.23 m for the energy interval 90 to 160 MeV. The angular distributions of the scattering events are given and also the distribution of energy losses $\Delta E/E$ for inelastic events. We try to interpret the results according to the optical model of the nucleus, assuming that the elastic scattering is due to a coherent scattering by the coulomb potential with a real nuclear potential, while inelastic scattering is considered as due to collisions of the K's with single nucleons. In this case one can try to derive the angular distribution of the inelastic cross section in the center-of-mass of the system K-nucleon.

M. BALDO-CEOLIN. Vedi pag. 464.

C. BALLARIO, R. BIZZARRI, B. BRUNELLI, A. DE MARCO, E. DI CAPUA, A. MICHELINI e G. MONETI (*Roma*). — **Studio del V^0 con camera di Wilson.**

Si descrivono i risultati dell'analisi di un gruppo di particelle instabili V^0 fotografate in una camera di Wilson al Laboratorio della Testa Grigia (3500 m s.l.m.). La camera ha un volume utile di $30 \times 35 \times 20$ cm³ e contiene 4 setti di ferro spessi 12 mm. Si sono ottenuti 30 000 fotogrammi con 220 V^0 e 6 produzioni associate di V^0 . L'analisi è stata compiuta classificando le V^0 in A^0 e 0^0 . La possibilità di V anomale è stata normalmente trascurata.

I. BARDUCCI (*Roma*). — **Dipendenza dei parametri elastici ed anelastici dalla concentrazione nelle leghe antimonio-bismuto.**

Si riferisce sui risultati di una ricerca sperimentale eseguita sulle leghe binarie antimonio-bismuto, allo scopo di studiare la dipendenza dei principali parametri elastici e dell'attrito interno dalla concentrazione dei due componenti puri. Oltre la densità, sono stati misurati: il modulo elastico longitudinale e quello torsionale, la velocità delle onde estensionali, quella delle onde trasversali ed il decremento logaritmico delle oscillazioni. Le misure sono state eseguite a temperatura ordinaria, prima e dopo un conveniente trattamento termico, e, per alcuni parametri anche a temperature elevate, fino a 200°—300 °C. La presente indagine sperimentale rientra in un più vasto programma di ricerche sui parametri elastici ed anelastici delle leghe binarie, e costituisce un caso, in certo senso, complementare rispetto a quello del sistema argento-oro, che è stato già considerato in un precedente lavoro da I. BARDUCCI ed L. VERDINI. Sebbene, infatti, i due sistemi Sb-Bi ed Ag-Au abbiano lo stesso tipo di diagramma di stato, con completa miscibilità per tutte le concentrazioni, i principali parametri fisici dell'antimonio e del bismuto hanno però valori molto diversi, a differenza di quanto avviene per i due componenti puri argento ed oro. Il confronto dei risultati ottenuti sui due sistemi consente, pertanto, di arrivare a conclusioni abbastanza generali sulle leghe binarie con miscibilità completa allo stato solido. Di particolare interesse appare il fatto che la dipendenza delle velocità e dei moduli elastici dalla concentrazione sembra discostarsi pochissimo dalla legge lineare anche per il sistema Sb-Bi, sebbene esista la già accennata differenza di caratteristiche dei due componenti e sebbene il trattamento termico non sia stato così prolungato da assicurare una conveniente omogenizzazione di tutte le leghe.

I. BARDUCCI (*Roma*). — **Sul comportamento anelastico dei solidi ad alta temperatura.**

La dissipazione interna di energia elastica nei solidi, alle temperature elevate, è stata oggetto di numerose ricerche sperimentali. Per quanto si riferisce alla giustificazione teorica dei fatti osservati, dopo una prima indagine di P. G. BORDONI ed M. NUOVO la questione è stata ripresa da W. P. MASON. Le due teorie cui si è accennato prevedono concordemente un accrescimento esponenziale del decremento logaritmico, in funzione dell'inverso della temperatura assoluta ed al crescere di questa; le conclusioni sono invece diverse circa la dipendenza del decremento dalla frequenza.

Mentre, infatti, BORDONI e NUOVO avevano previsto una proporzionalità inversa alla frequenza, il decremento risulta invece indipendente da questa nella teoria di MASON. Data l'insufficienza dei risultati sperimentali finora noti, si è pertanto ritenuto opportuno procedere ad una verifica sperimentale su materiali nei quali l'effetto in questione non è mascherato da altre cause di dissipazione, ed in particolare da fenomeni di rilassamento elastico. I risultati confermano pienamente la dipendenza esponenziale del decremento dalla temperatura; circa l'effetto legato alla frequenza, essi suggeriscono un comportamento intermedio fra quelli previsti dalle due teorie, sebbene più prossimo alle conclusioni di MASON.

A. BARONE, G. PISENT e D. SETTE (Roma). — Misure di velocità di propagazione degli ultrasuoni in liquidi soprafusi.

Esperienze fatte su alcuni liquidi, che possono essere facilmente portati allo stato soprafuso, hanno dimostrato che talune grandezze fisiche presentano un comportamento anomalo, quando si passa dallo stato di fusione allo stato di soprafusione. DODD e HU PAK MI ⁽¹⁾ hanno eseguito misure di viscosità su metacloronitrobenzolo ed etere di fenile. Essi hanno trovato che l'energia di attivazione che compare nella formula di Andrade per la viscosità, è maggiore nello stato di soprafusione. DODD e ROBERTS ⁽²⁾ hanno misurato la costante dielettrica del salolo, mentolo ed etere di fenile. Questi risultati fanno pensare ad una variazione strutturale in seno al liquido. Si può quindi prevedere un comportamento anomalo anche nell'andamento della compressibilità e quindi della velocità di propagazione di onde elastiche, in funzione della temperatura. HUNTER ⁽³⁾ ha eseguito misure di velocità nel mentolo con un metodo ad impulsi (68 MHz) ed ha infatti trovato che passando attraverso il punto di fusione cambia il coefficiente di temperatura relativo alla velocità. PETRALIA e CEVOLANI ⁽⁴⁾ hanno eseguito misure di velocità sul salolo con un metodo interferometrico (600—3000 kHz) e, entro i limiti dell'approssimazione denunciata, (1 su 1000) non hanno riscontrato alcuna discontinuità in corrispondenza al punto di fusione. Nella presente ricerca si è usato un nuovo tipo di interferometro, studiato da uno degli Autori ⁽⁵⁾, per eseguire misure di velocità su tutti e quattro i liquidi sopra citati. L'interferometro funziona alla frequenza di 4 MHz e consente una elevata sensibilità (dell'ordine dell'1 per 10000). Si sono ottenuti i seguenti risultati: nel mentolo, etere di fenile e m-cloronitrobenzolo, si riscontra una discontinuità nell'inclinazione della retta velocità-temperatura, in vicinanza del punto di fusione. Il coefficiente di temperatura è leggermente maggiore nella zona di soprafusione. Tale risultato è in accordo con quello ottenuto da Hunter. Nel salolo invece, non si nota una variazione apprezzabile del coefficiente di temperatura, ma la curva della velocità presenta un flesso nell'intorno del punto di fusione. Poiché questa anomalia è molto piccola, è facile spiegarsi perché il fenomeno non sia rivelabile con metodi di minore sensibilità.

⁽¹⁾ C. DODD e HU PAK MI: *Proc. Phys. Soc. London*, B **62**, 454 (1949).

⁽²⁾ C. DODD e G. ROBERTS: *Proc. Phys. Soc.*, B **63**, 814 (1950).

⁽³⁾ A. H. HUNTER: *Proc. Phys. Soc.*, B **64**, 1086 (1951).

⁽⁴⁾ M. CEVOLANI e S. PETRALIA: *Ric. Scient.*, **21**, 1623 (1951).

⁽⁵⁾ A. BARONE: *Rendiconti del Congresso degli Ultrasuoni* (Marsiglia, 1955).

F. BELLA (Roma), S. FOCARDI, C. RUBBIA e G. TORELLI (Pisa). – Metodi di comando rapido di rivelatori di tracce.

Uno dei problemi pratici che si presenta frequentemente in esperienze di fisica nucleare è quello di disporre di impulsi di tensione di brevissima durata (dell'ordine del millimicrosecondo) con rapidi fronti di salita. Questi impulsi vengono formati in seguito al verificarsi di un certo evento fisico: per es. il passaggio di una particella ionizzante attraverso un opportuno rivelatore. L'intervallo di tempo τ che intercorre fra l'inizio dell'impulso di tensione e il verificarsi dell'evento al quale tale impulso è associato dipende dalla natura del rivelatore e dal sistema con cui l'impulso viene formato. Di regola non è necessario preoccuparsi di rendere τ particolarmente breve, ma basta assicurarsi che esso si conservi costante entro limiti convenientemente ristretti. In qualche caso, tuttavia, può essere essenziale che τ sia il più breve possibile. Ciò accade per esempio, quando si desidera « comandare » un rivelatore di tracce che rimane sensibile finché non sia avvenuta la ricombinazione degli ioni in esso liberati dall'evento. Il presente lavoro riguarda alcuni nuovi metodi di coincidenza adatti appunto per conseguire un rapidissimo comando di rivelatori di tracce quali la camera odoscopica ⁽¹⁾, la camera a bolle, ecc. In uno dei metodi che verranno descritti si fa uso di contatori piani, del tipo sviluppato da BELLA e FRANZINETTI ⁽²⁾, disposti in serie con le tensioni di lavoro opportunamente regolate. Con un dispositivo di tale genere è possibile ottenere impulsi di ampiezza superiore a 1000 V in corrispondenza di una coincidenza, facilmente separabili dagli impulsi singoli (alcune centinaia di volt). Il ritardo di tali impulsi rispetto al passaggio della particella attraverso i contatori è dell'ordine di 10^{-8} s. Si sta studiando, inoltre, la possibilità di comandare direttamente con due distinti contatori, le due griglie di una valvola 715 B, in modo da ottenere impulsi di coincidenza di 15 kV con un ritardo di circa $5 \cdot 10^{-8}$ s rispetto all'evento. In un terzo metodo si utilizzano due contatori piani in opposizione, (per es. facendoli lavorare con tensioni di opposta polarità) in modo da ottenerne il comando di una piccola camera odoscopica in tempi confrontabili con i tempi di salita degli impulsi dei contatori stessi. Il medesimo metodo potrebbe essere applicato per comandare (sostanzialmente secondo il criterio suggerito da G. MARTELLI ⁽³⁾ e coll.) una camera a liquido tenuta in condizione di bassa sensibilità.

⁽¹⁾ M. CONVERSI e A. GOZZINI: *Nuovo Cimento*, **2**, 189 (1955).

⁽²⁾ F. BELLA e C. FRANZINETTI: *Nuovo Cimento*, **10**, 1461 (1953).

⁽³⁾ L. BERTANZA, P. FRANZINI, G. MARTELLI e B. TALLINI: presentato al *Cern Symp.* (11-23 Giugno 1956).

G. BERTOLINI, M. BETTONI e E. LAZZARINI (Milano). – Correlazioni angolari fra i raggi γ da 1.24 MeV e 0.845 MeV del ^{56}Fe .

È stato studiato il decadimento del ^{56}Co con uno spettrometro a scintillazione e con uno spettrometro magnetico. È stato verificato che tra i vari decadimenti del ^{56}Co (emissione β^+ e cattura K) uno di questi consiste in un decadimento β^+ di $E_{\text{max}} \simeq 1.5$ MeV su di uno stato eccitato del ^{56}Fe di $E = 2.085$ MeV. Questo livello si diseccita con emissione di due raggi γ in cascata di energia 1.24 MeV e 0.845 MeV.

Si è quindi misurata la correlazione angolare tra i gamma emessi dal ^{56}Fe in coincidenza con i β^+ dello spettro di $E_{\text{max}} \simeq 1.5$ MeV. La funzione di correlazione trovata, corretta per la geometria finita, è: $W(\theta) = 1 + (0.1023 \pm 0.0027)P_2(\cos \theta) + (0.0015 \pm 0.0035)P_4(\cos \theta)$. Tale risultato è in accordo con un assegnazione di spin 2 e 4 ai due livelli del ^{56}Fe di energia pari a 0.845 e 2.085 MeV, assumendo zero lo spin dello stato fondamentale del ^{56}Fe .

B. BERTOTTI (*Dublin*). — Sul moto gravitazionale.

Il problema dell'interazione gravitazionale può venire utilmente attaccato mediante un procedimento perturbativo invariante per ogni trasformazione di Lorentz, in cui la consueta ipotesi di «quasi stazionarietà» è sostituita da una più generale. Una conveniente distribuzione regolare di energia e di momento si presta alla descrizione dei corpi in gioco, che si assumono dotati di una semplice e rigorosa proprietà di simmetria sferica. Le equazioni di moto che così si ottengono nel primo stadio di approssimazione e in una maniera assai semplice, coincidono con quelle di Einstein, eccezion fatta per i due termini che non sono lineari nelle masse.

M. BETTONI. Vedi pag. 435.

M. BICHARA (*Johannesburg*). — Risultati di un oscillatore con transistor.

L'autore utilizza un transistor a punta per un oscillatore il quale al funzionamento si è distinto per il fatto che, senza particolari precauzioni, la frequenza varia di solo $\pm 0.0055\%$ quando il voltaggio di alimentazione varia del 44%; tale stabilità è ottenuta senza uso di termistori od altri componenti non lineari.

N. N. BISWAS, L. CECCARELLI-FABBRICHESI, M. CECCARELLI, K. GOTTSTEIN, N. C. VARSHNEYA and P. WALOSCHEK (*Göttingen*). — Nuclear Scattering of Positive K-Mesons in the Energy Region of 80 MeV.

A number of interactions of K^+ -mesons having energies between 60 and 100 MeV with the nuclei of photographic emulsion are analysed. From a comparison of the angular and energy loss distributions of the scattered K^+ -mesons with the results of a Monte Carlo calculation, performed with the assumption of an independent particle model of a nucleus, it has been attempted to derive informations about the behaviour of the K^+ -nucleon cross-section. Though the model used is certainly oversimplified, it has been possible to establish that the behaviour of the K^+ -nuclei collisions is not inconsistent with the assumptions that the elementary K-nucleon cross-section has a preferentially s-wave scattering and that the K^+ -meson experiences a repulsive nuclear potential. This is also consistent with the data on the scattering of K^+ -mesons with free hydrogen nuclei, which are also presented.

N. N. BISWAS, L. CECCARELLI-FABBRICHESI, M. CECCARELLI, K. GOTTSTEIN, N. C. VARSHNEYA and P. WALOSCHEK (*Göttingen*). – **Scattering of K^+ -Mesons on Light Nuclei.**

Among the scatterings of K-mesons with the nuclei of photo-emulsion a number of events have been demonstrated to be due to the collisions with light nuclei. For some of these events an analysis in terms of known nuclear reactions (^{12}C tripartition) is consistent. From the study of these events it is possible to understand the limitation of the treatment of a nucleus as an independent particle model.

N. N. BISWAS, L. CECCARELLI-FABBRICHESI, M. CECCARELLI, K. GOTTSTEIN, N. C. VARSHNEYA and P. WALOSCHEK (*Göttingen*). – **Some Remarks on the τ and θ Decay.**

A discussion is made on several experimental results of the Göttingen group and of other laboratories in connection with the problem of reconciling the τ and θ decays with the decay of a single heavy meson of definite spin and parity. The existence of some rather firmly established contradictions against this hypothesis seems to lead to the postulation that the parity is not conserved in weak interactions.

N. N. BISWAS, L. CECCARELLI-FABBRICHESI, M. CECCARELLI, K. GOTTSTEIN, N. C. VARSHNEYA and P. WALOSCHEK (*Göttingen*). – **The Properties of the τ -Decay.**

The usual Dalitz analysis is made for an unbiased sample of τ -meson. It is concluded that the data are not consistent with the decay of an even spin and even parity particle. The study of polarization effects supports, in addition, the view that the spin of heavy mesons is equal to zero thus making impossible to reconcile the τ - and θ -decay with the decay of a single particle of defined spin and parity. Data are also presented on the probable asymmetry in the spectrum of π^- emitted in the τ -decay, on the $K_{\pi 3}$ secondaries spectrum and on some examples of τ - and τ' -decays in flight.

R. BIZZARRI. Vedi pag. 433.

A. BONETTI. Vedi pag. 464.

V. BORELLI, L. FERRETTI, R. GESSAROLI, L. LENDINARA, A. CHIARINI, A. TOMASINI, G. QUARENI, A. RANZI e G. PUPPI (*Bologna*). – **Interazione con i nuclei dei mesoni π positivi e negativi d'energia tra 0 e 130 MeV.**

Sono stati osservati in lastre fotografiche numerose interazioni nucleari dovute a mesoni π^\pm di energia tra 0 e 130 MeV. Le emulsioni erano state esposte ai pioni prodotti col sincrociclotrone di Chicago. Sono stati determinati i liberi cammini medi d'interazione in funzione dell'energia. Gli eventi sono stati analizzati e particolare attenzione è stata posta agli scattering anelastici. Per questi eventi sono state

determinate la distribuzione angolare e quella energetica dei pioni diffusi. Si cerca di interpretare il fenomeno, assumendo un modello nucleare a gas di Fermi ed assumendo che nella materia nucleare si mantengano le proprietà dello scattering dei pioni contro i nucleoni liberi. Appare però abbastanza evidente che per la interpretazione del fenomeno ed in particolare delle perdite di energia dei pioni si debba tener conto del potenziale nucleare che agisce sui mesoni π . I relativi calcoli sono in corso di esecuzione.

E. BORELLO. Vedi pag. 458.

D. BRINI, L. PELI, O. RIMONDI e P. VERONESI (*Bologna*): — **Sul rapporto di di asimmetria nell'effetto fotoelettrico prodotto da fotoni polarizzati.**

Applicando al caso specifico l'equazione d'onda relativistica di Dirac, SAUTER ha calcolato, nell'approssimazione $\alpha Z \ll 1$, la sezione d'urto differenziale dell'effetto fotoelettrico prodotto da fotoni polarizzati linearmente. I calcoli di Sauter sono stati effettuati tenendo conto unicamente dei processi che interessano lo strato K che nel totale rappresenterebbero solo l'80% degli eventi fotoelettrici. Partendo da questi risultati e nell'intento di verificarli W. H. Mc MASTER e F. L. HEREFORD hanno effettuato un esperimento nel quale, dopo avere polarizzato un fascio di raggi γ del ^{60}Co mediante uno scattering Compton, hanno studiato l'effetto fotoelettrico prodotto dai fotoni polarizzati. L'esperimento è stato condotto determinando il rapporto fra le frequenze dell'effetto fotoelettrico misurate rivelando i fotoelettroni prima nel piano di scattering e poi nel piano normale. Si può dimostrare che tale rapporto è strettamente legato alla sezione d'urto differenziale dell'effetto fotoelettrico dovuto a fotoni polarizzati linearmente. I risultati degli autori citati, sono stati ottenuti supponendo isotropo il contributo dei fotoelettroni di tutti gli strati diversi dal K . Il nostro esperimento è stato progettato e condotto allo scopo di svincolare la misura da questa ipotesi e con l'intento di rivelare solo gli eventi fotoelettrici interessanti lo strato K . A questo proposito l'evento in esame veniva riconosciuto, rivelando il quanto X emesso dall'atomo che ha subito l'effetto fotoelettrico, in coincidenza con la rivelazione del fotoelettrone corrispondente. Un discriminatore opportuno, assicurava che il quanto X corrispondesse al salto di un elettrone dello strato K . Le nostre misure del rapporto di asimmetria sono state eseguite per diverse energie dei fotoni polarizzati (ottenute con scattering Compton a diversi angoli dei γ del ^{60}Co , ai quali corrispondono diversi stati di polarizzazione dei fotoni) ed usando come elemento sul quale si studiava l'effetto fotoelettrico il Pb. I risultati non sono stati ancora completamente elaborati. È possibile tuttavia, già da ora, prevedere un soddisfacente accordo con le previsioni teoriche.

R. BRUNELLI. Vedi pag. 433.

G. CARERI e J. REUSS (*Frascati*). — **Il laboratorio criogenico del Sincrotrone Nazionale.**

Viene illustrato il laboratorio criogenico fornito di un liquefattore di elio e idrogeno, della potenzialità di otto litri per ora. Vengono mostrate le modalità con cui gruppi di Università Italiane potranno effettuare esperienze nel laboratorio stesso, ed anche trasportare quantitativi di elio liquido nella propria sede.

A. CARRELLI e F. CENNAME (Napoli). — Misure del secondo coefficiente di viscosità dell'acqua a varie frequenze.

Sono continuate le misure per la determinazione del vento ultrasonoro, che può essere connesso con il secondo coefficiente di viscosità dei liquidi. La determinazione della velocità del vento era fatta, come già detto in un lavoro precedente, mediante l'immissione di un filetto di liquido colorato con velocità normale a quella del vento. Le misure sono state limitate all'acqua per frequenze fra 1.8 ed 6.6 MHz. Dalla analisi accurata dei risultati sperimentali si può concludere che il rapporto fra i due coefficienti, diviso il quadrato della frequenza, può considerarsi quasi costante entro questo campo di frequenze.

A. CARRELLI e R. DELLA CAGGIA (Napoli). — Misure di costante dielettrica di soluzioni di sostanze proteiche in acqua in alta frequenza.

È ben noto che alcune sostanze proteiche in soluzione acquosa sono soggette ad elettroforesi e quindi portano cariche elettriche. Si è voluto ricercare se l'aggiunta di tali sostanze proteiche in soluzioni debolmente conduttrici produce una diminuzione della costante dielettrica. Si è proceduto alla misura della costante dielettrica in queste soluzioni ad alta frequenza secondo un metodo già elaborato, e si è notato che esiste un comportamento specifico molto marcato a seconda delle varie sostanze relativamente al valore di detta costante.

A. CARRELLI e F. GAETA (Napoli). — Un nuovo metodo per la determinazione del coefficiente di assorbimento ultracustico nei liquidi.

Il nuovo metodo proposto per la determinazione del coefficiente di assorbimento degli ultrasuoni, consiste nella determinazione dell'intensità del reticolo ultrasonoro in funzione del tempo, quando in un sistema di onde stazionarie venga interrotta l'eccitazione del quarzo. In questa prima serie di misure la determinazione della variazione di intensità è stata fatta con un metodo fotografico. I valori finora trovati per il coefficiente d'assorbimento nei liquidi: acqua, alcool etilico, alcool isopropilico e benzolo, sono certamente superiori a quelli teorici, ma nel caso del benzolo nettamente inferiori a quelli ottenuti dagli altri sperimentatori.

A. CARRELLI, F. GAETA e G. COZZA (Napoli). — Ricerca dell'effetto Debye in soluzioni colloidali in campi acustici.

Secondo un calcolo sviluppato da Debye, in una soluzione elettrolitica percorsa da onde ultracustiche, nasce una differenza di potenziale che, utilizzando sorgenti normali di ultrasuoni, deve essere dell'ordine di almeno 10^{-6} V. Alcuni sperimentatori hanno affermato che usando soluzioni colloidali, in cui si hanno granuli elettrizzati di massa molto maggiore, l'effetto deve essere molto più vistoso, ed esperienze da loro eseguite danno infatti differenze di potenziale dell'ordine dei decimi di volt. Sono state ripetute le stesse esperienze e le misure corrispondenti sono state condotte con

molta cura. Le soluzioni colloidali usate sono: argento colloidale e soluzioni di gelatina in acqua a varie concentrazioni. Le sonde poste nel mezzo percorse da ultrasuoni erano collegate ad un amplificatore per la frequenza dell'onda ultrasonora e cioè 1.8 MHz. La corrente d'uscita dall'amplificatore viene opportunamente raddrizzata, e l'intensità della corrente letta (con un apparecchio capace di rivelare 10^{-6} A). Non è stata trovata finora nessuna traccia dell'effetto affermato dai ricercatori olandesi.

A. CARRELLI e A. GRIECO (Napoli). – Misure della velocità delle onde termiche nei liquidi mediante sospensione trifilare.

Sono continuate le misure sulla velocità delle onde termiche nei liquidi ed è stato adoperato quale misuratore delle forze, invece della bilancia una sospensione trifilare che ha il vantaggio, in opportune condizioni, di una maggiore sensibilità, e di una maggiore prontezza ($2 \div 3$ s). Le misure sono state compiute relativamente ad un gas, l'aria, e per diversi liquidi, ritrovando quale valore di detta velocità nei liquidi valori che si accordano con quelli ottenuti da R. Lucas.

A. CARRELLI e W. MANCINI (Napoli). – Misure della costante dielettrica in soluzioni elettrolitiche mono- bi- e trivalenti di alta frequenza.

In un opportuno circuito di risonanza ad alta frequenza, in cui è posta come resistenza una soluzione elettrolitica, sono state misurate le variazioni della costante dielettrica dell'acqua per la presenza di ioni. Riportando le variazioni della costante dielettrica in funzione della concentrazione, si osserva che esse crescono man mano che si passa dagli ioni monovalenti agli ioni tetravalenti. È da notare ancora che l'aggiunta in queste soluzioni di particelle atte a generare la persistenza dei reticoli ultrasonori produce un'ulteriore variazione della costante dielettrica, il che dimostra in altro modo il supposto addensamento dei dipoli dell'acqua intorno ai granuli.

A. CARRELLI e F. PORRECA (Napoli). – Determinazione della diminuzione di intensità del reticolo ultracustico in soluzioni colloidali.

Per la misura della legge di caduta dell'intensità al cessare degli ultrasuoni in una soluzione colloidale la luce, opportunamente modulata, viene fatta cadere su di una cellula fotoelettrica, la quale è collegata con un oscillografo. La figura all'oscillografo viene ingrandita e le deviazioni del pennellino elettronico vengono misurate in funzione del tempo. Si è potuto in tal modo stabilire che la legge di caduta è una legge esponenziale, e che il parametro che da tale legge deriva dipende dalla natura del liquido usato, e della sostanza contenutavi.

A. CARRELLI e E. TARTAGLIONE (Napoli). – Un'esperienza che permette la misura diretta del secondo coefficiente di viscosità.

L'esperienza realizzata consiste nel disporre una sfera di caucciù, piena del liquido in esame, in un cilindro in cui la pressione varia sinusoidalmente; si realizza in tal modo una sfera pulsante. Si prevede che nella massa di liquido contenuta nella

sfera si debba produrre un aumento della temperatura e che tale aumento debba essere proporzionale a $(2\mu - 3\lambda)$, dove λ è il secondo coefficiente di viscosità, al quadrato del $\Delta\rho$ e alla pulsazione ω . Sono stati effettivamente misurati notevoli aumenti di temperatura con comportamenti diversi da liquido a liquido (acqua, benzolo, tetracloruro di carbonio, solfuro di carbonio) ed è stata riscontrata effettivamente una proporzionalità con ω . Non può però ancora dirsi che si possa giungere ad un risultato conclusivo relativamente al secondo coefficiente.

J. M. CASSELS. Vedi pag. 451.

C. CASTAGNOLI, C. FRANZINETTI and A. MANFREDINI (*Roma*). — **On Parity Conservation in Weak Interactions and angular Distribution in $\pi \rightarrow \mu \rightarrow e$ Decays.**

It has been suggested by LEE and YANG (T. D. LEE and C. N. YANG: *Phys. Rev.*, **104**, 254 (1956)) that parity was not necessarily conserved in weak interactions. If parity conservation is violated in decay processes as for instance the $\pi \rightarrow \mu + \nu$ and the $\mu \rightarrow e + 2\gamma$ decays, then the angular distribution of the electron with respect to the direction of motion of the μ -meson in the system in which the π is at rest, should depart from isotropy. Experimental data based on 410 $\pi \rightarrow \mu \rightarrow e$ decays in emulsions exposed to cosmic rays indicate that if the distribution is asymmetric, the asymmetry is small:

$$\alpha = 2 \frac{N_{\text{forward}} + N_{\text{backward}}}{N_{\text{forward}} - N_{\text{backward}}} = -0.13 \pm 0.10$$

In a recent paper LEE and YANG noticed that the hypothesis of parity conservation in weak interactions (β -decays, meson and hyperon decays, etc.) is not supported by any experimental evidence, and that, on the other hand, if parity need not be conserved, 0^+ and τ^+ may be identified as the same particle. To decide the question they suggested several experiments and in particular the study of the angular distribution of the electron with respect to that of the μ -meson in π - μ - e decays. If parity conservation is violated in both processes, (π - μ decay and μ - e decay) the μ -meson would be polarized in the direction of its motion in the system in which the π is at rest. Consequently the distribution of the angles ω (this being the angle between the direction of motion of the μ when emitted from its parent π at rest and that of the electron when emitted from the μ decay) should be asymmetric with respect to the $\omega = \pi/2$ plane. In the present note we report on an attempt to reveal such an asymmetry if it exists.

We have examined all the π - μ decays (from π 's at rest) which had been observed in 600 μ m emulsion exposed to cosmic rays. We have selected 410 events which satisfied the following conditions: a) the μ -meson decayed in the same emulsion in which it was created; b) the projection of the electron track on the plane of the emulsion was $\geq 20 \mu$ m; c) both the μ and the electron formed an angle with the plane of the emulsion of less than 68° , to allow a precise angular determination. In none of the cases considered the error associated with the measurement of ω was larger than 2° . The data have been corrected for geometrical biases due to conditions a), b) and c) which introduce asymmetrical losses in the angular intervals $0 \div \pi/2$ and $\pi/2 \div \pi$ with a maximum around 90° . Let us consider the parameter α defined by the equation

$$\alpha = 2 \frac{N_f + N_b}{N_f - N_b}$$

where N_f represents the number of events associated with a value of $0 \leq \omega \leq \pi/2$ and N_b having $\pi/2 \leq \omega \leq \pi$. Obviously for isotropy one gets $\alpha=0$. We get $\alpha = -0.13 \pm 0.10$. An identical value has been obtained by determining α using the least squares method. This result does not exclude an asymmetric distribution but does not suggest a strong asymmetry. In order to determine it more statistical data are required. Research on this line has already been started in this laboratory.

M. CECCARELLI. Vedi pag. 436, 437.

L. CECCARELLI-FABBRICHESI. Vedi pag. 436, 437.

F. CENNAMO. Vedi pag. 439.

C. CEOLIN and L. TAFFARA (*Padova*). – **On the Scattering of K-Mesons by Nucleons.**

Using the method of Feynman, and considering both the Σ and the Λ as intermediate states, the differential and total cross sections for the scattering of scalar and pseudoscalar K^+ -mesons by nucleons have been calculated in second order approximation of perturbation theory. It is found that the ratio:

$$\frac{\text{Process with charge exchange}}{\text{Process without charge exchange}},$$

is equal to unity if only the Λ particle participates in the intermediate state, to one fifth if only the Σ participates, and is very much less than one fifth if both the Λ and the Σ intervene with the same coupling constant. In this way, within the limits of validity of the perturbation theory calculation and of the few experimental results so far available, it would seem that only the Σ contributes to the intermediate states. As far as the ratio K^+N/K^+P is concerned, it turns out to be (only in this second order approximation) 4 with only the Σ , zero with only the Λ and roughly equal to one if both the Λ and Σ are involved. These results are discussed in relation to a theory in which only one of the two states of total isotopic spin is important in the process of scattering considered.

A. CHIARINI. Vedi pag. 437.

G. COCCONI, G. PUPPI, G. QUARENI e A. STANGHELLINI (*Bologna*). – **Sull'interazione nucleare dei mesoni K^+ .**

Sono stati presi in considerazione i risultati ottenuti in vari laboratori (Berkeley Bologna, Bristol, Göttingen, Padova) sulla interazione dei mesoni K^+ con l'idrogeno e con gli altri nuclei che compongono le emulsioni fotografiche. L'intervallo

energetico considerato va da 50 a 130 MeV. Le principali caratteristiche dell'interazione si possono così riassumere: a) La sezione d'urto totale $K^+ + P = K^+ + P$ è di circa 14 mb. La sezione d'urto differenziale appare leggermente in avanti nel sistema del centro di massa e può essere rappresentata sostanzialmente da un'onda S , con interferenza coulombiana costruttiva. Si può proporre un modello di interazione supponendo che il protone si comporti come una sfera perfettamente riflettente di raggio $a \sim h/m_K c$. Questo modello rende conto delle sezioni d'urto totale e differenziale osservata. b) Dall'analisi degli urti anelastici osservati nelle interazioni con i nuclei si deduce che il potenziale nucleare che agisce sui mesoni K^+ è repulsivo e dell'ordine di 10 MeV. c) La stessa analisi permette di dedurre la sezione d'urto differenziale media dei mesoni K^+ con i protoni e neutroni nei nuclei. Essa risulta prevalentemente all'indietro. Sottraendo a questa sezione d'urto media il contributo dei protoni, si ottiene per il processo $K^+ + n = K^+ + n$ una sezione d'urto differenziale marcatamente all'indietro. d) Dalle sezioni d'urto elementari [paragrafi a) e c)] è possibile dedurre col modello ottico un potenziale nucleare medio in accordo con quello menzionato nel paragrafo b). e) Il potenziale nucleare medio e quello coulombiano permettono di interpretare anche il comportamento degli urti elastici dei mesoni K^+ contro i nuclei.

A. M. CONFORTO. Vedi pag. 431.

M. DI CORATO. Vedi pag. 431.

G. COSTA and G. PATERGNANI (Padova). — The Elastic Scattering of K^+ in Nuclei According to the Optical Model.

The elastic scattering of K^+ -mesons in nuclei has been studied, the interaction K^+ -nucleus being described by means of the optical model with a constant complex potential. From the experimental data at present available on the inelastic interaction of K^+ , the imaginary part would seem to be of a few MeV, and so for the calculation of the elastic scattering at energies which are not too low, it may be put equal to zero. In the external region of the nucleus the real part coincides with the coulomb potential; in the internal region the nuclear potential must be added to that due to a uniform distribution of the electrical charge. In order to determine the value of the nuclear potential, the total elastic collision cross section (from 20° to 180°) has been calculated as a function of the potential for various energies in the interval -20 to $+15$ MeV. For a given value of the experimental elastic cross section one has, however, in this way, two values for the nuclear potential: one attractive and one repulsive which is less in absolute value. For this reason the shape of the cross section at small angles has been studied (10° to 20°): in this angular interval there is a marked interference between the nuclear and coulomb potentials, which is constructive or destructive according to the sign of the nuclear potential; from a comparison with experimental data one may decide between the two possibilities. To determine the sign of the potential, and to test the consistency of the model, the nuclear potential has been calculated by means of a certain type of elementary interaction K^+ -nucleon; for the same type of interaction the total inelastic cross section has been

calculated by means of perturbation theory. The ratio between the elastic and inelastic cross sections so obtained is different according to whether the potential is attractive or repulsive, and so it will perhaps be possible to discriminate between the two possibilities.

G. COZZA. Vedi pag. 439.

M. CRESTI, W. D. B. GREENING, L. GUERRIERO, A. LORIA and G. ZAGO (*Padova*). — **Inelasticity in Collisions between Pions and Lead Nuclei.**

Si riferisce su di una misura compiuta al Laboratorio della Marmolada con un dispositivo costituito da una Camera di Wilson a campo magnetico sovrapposta ad una a setti. L'energia di pioni carichi prodotti in reazioni nucleari causate dalla radiazione cosmica in un generatore di piombo viene misurata nella camera superiore. Quando essi interagiscono nei setti di piombo della camera inferiore l'energia dei pioni neutri prodotti viene valutata dallo studio delle cascate elettrofotoniche di decadimento. Si determina quindi il coefficiente di anelasticità, definito come rapporto fra l'energia dei pioni presenti dopo la reazione e quella totale del pione incidente. Il suo valor medio risulta 0.5: si ha preferenza per valori vicini a zero e ad uno. I risultati si inquadrano bene nella letteratura sperimentale e teorica sull'argomento e possono essere interpretati pensando che le interazioni di pioni con nuclei pesanti debbano dividersi in due classi abbastanza distinte, una delle quali comprende urti centrali e l'altra urti periferici.

M. CRESTI. Vedi pag. 432.

G. CRISTIANI, A. LOVATI and M. PANETTI (*Milano*). — **Progetto di un analizzatore magnetico di particelle di 1 GeV.**

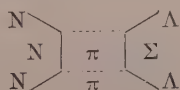
Fra i diversi problemi il cui studio potrà essere affrontato con le tecniche dei contatori e delle camere (a nebbia, a bolle, ...) al sincrotrone per elettroni da 1 GeV in costruzione a Frascati, rivestono particolare importanza due tipi di esperimenti: 1) quelli collegati alla produzione di pioni e particelle K dal fascio dei gamma primari e 2) quelli relativi allo scattering degli elettroni estratti dal sincrotrone. In ambedue i casi si prevede la necessità di impiegare sistemi focalizzatori ed analizzatori di alta qualità: nelle esperienze del primo tipo occorre inoltre tener presente la instabilità delle particelle, che impone cammini piuttosto brevi fra sorgente e rivelatore. Nella presente relazione si riferisce lo studio di un sistema costituito da due lenti magnetiche a quadrupolo e da un magnete rettangolare di grandi dimensioni. Vengono indicati i calcoli svolti per valutare le traiettorie delle particelle, l'ingrandimento, il potere dispersivo, il flusso trasmesso, ecc., nonché le caratteristiche meccaniche ed elettriche del sistema.

K. M. CROWE (*Stanford, California, U.S.A.*). — **The Masses of Light Mesons, K Mesons, and Hyperons in 1956.**

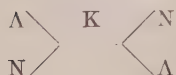
A number of independent accurate measurements of the masses of light mesons has been critically reviewed. Assuming the positive- and negative-charged mesons to have equal masses, best values for the pion and muon masses can be calculated. It is found that the negative π^- and μ^- -mesic X-ray energies measured by K absorption edges can be combined with the mass difference between the positive pion and muon to give a result with a standard deviation approximately one third of the assigned errors of the best previous measurement. All the results are in satisfactory agreement and can be combined in the usual way. The mass results are as follows: $M_\mu = (206.86 \pm 0.11) m_e$; $M_\pi = (273.27 \pm 0.11) m_e$. Experimental data on the mean lives, spins, parities, and decay modes have also been reviewed and the results will be given. The measurements of the masses of the various K-mesons are obtained in several ways: $M_{K\pi^2} = (306.0 \pm 1.5) m_e$; $M_{K\mu^2} = (965.3 \pm 1.9) m_e$; $M_\tau = (966.8 \pm 0.4) m_e$. There is at present no evidence for a difference in the masses to a precision of $1 \div 2 m_e$. Results on the $K_{\mu^2}^+$, $K_{\pi^2}^+$ and τ^+ masses and lifetimes and the analysis of τ^+ decay will be discussed. At present the experimental equality of these particles seems to be contradictory to assigning a spin of less than 2. The cosmic-ray data on the θ^0 lifetime are reviewed and recent results on artificially-produced θ^0 's will be discussed. The hyperon mass data will be reviewed. $M_{\Lambda^0} = (2181.74 \pm 0.35) m_e$; $M_{\Sigma^+} = (2327.4 \pm 1.0) m_e$. The latest data on a $\Sigma^+ - \Sigma^-$ mass difference and their mean lives will be presented.

N. DALLAPORTA e F. FERRARI (*Padova*). — **On the Λ -Nucleon Force and the Binding Energy of Light Hyperfragments.**

The problem of the binding of a Λ particle in nuclear matter to form the observed unstable hyperfragments has been already considered by different authors who generally try to explain the observed phenomena assuming that the force acting between Λ and nucleon is due to the K field according to the scheme: $\Lambda \rightarrow K + N$, $N \rightarrow K - \Lambda$. There is however no reason why the pion field should not be also effective in binding hyperons with nucleons; therefore in the present paper, a different approach to the problem is presented, consisting in assuming that both a pion and a K force are present between Λ and nucleon and trying to evaluate the relative strength of both by comparison with the known binding energies of light hyperfragments. Experimental evidence concerning at least the τ -meson favours spin 0, while recent work shows that probably the spin of the Λ is not greater than $\frac{3}{2}$. As nothing is known concerning the parities of hyperons, the calculations are done assuming the d'Espagnat and Prentki Hamiltonian and with both scalar and pseudovector coupling (spin of $\Lambda = \frac{1}{2}$). In order to preserve charge independence, the following schemes are assumed for the pion interaction:



and for the K interaction:



The calculations are conducted following the line of the Brueckner and Watson calculation for usual nuclear forces. The Λ -nucleon force turns out to be spin independent for scalar coupling, and repulsive in case of the pion force. Instead it is attractive in case of the pion force for pseudovector coupling and the singlet state is more attractive than the triplet one. The spin dependence of the forces already pointed out by Dalitz favours therefore pseudovector coupling. The light hyperfragments are considered as consisting of a normal nucleus (^2H , ^3H , ^3He , ^4He) to which the Λ is bound. In this approximation, it is found that for $^5\text{He}^\Lambda$ the mean value of the K force over singlet and triplet states vanishes, so that the binding should be due only to the pion force. Also in the other cases, the pion force seems to have a dominant part. A good fit to the experimental values for the binding energies is obtained if one assumes that the interaction constants for both the pion and the K force are of the same order of magnitude than the constant of the ordinary nuclear forces.

N. DALLAPORTA. Vedi pag. 432.

G. DASCOLA. Vedi pag. 453.

A. DEBENEDETTI, C. M. GARELLI, L. TALLONE M. VIGONE (*Torino*). — **Studio delle cascate elettromagnetiche nelle emulsioni nucleari.**

Studiando un notevole numero di cascate elettromagnetiche, abbiamo determinato l'andamento della molteplicità in funzione dell'energia del primario, lo spettro di energia delle coppie secondarie e la produzione di tridenti. Non abbiamo rilevato nessuna apprezzabile differenza dalle previsioni teoriche.

A. DEBENEDETTI, C. M. GARELLI, L. TALLONE e M. VIGONE (*Torino*). — **Una interazione nucleare di alta energia.**

Abbiamo determinato il $p\beta$ dei secondari di un getto di alta energia mediante misure di scattering. Abbiamo calcolato la distribuzione degli angoli e dei momenti nel sistema del baricentro trovando un buon accordo con le teorie di Heisenberg e di Wataghin. Diamo anche il valore della percentuale dei mesoni K emessi nell'interazione e quello del cammino libero medio per interazioni nucleari dei π carichi.

R. DELLA CAGGIA. Vedi pag. 439.

G. C. DELLA PERGOLA e D. SETTE (Roma). — Effetti galvanomagnetici nel germanio.

Si riferisce sui risultati di una serie di misure di effetto Hall e magnetoresistenza effettuate, a temperatura ambiente, su campioni monocristallini di germanio di tipo «p» (di resistività compresa fra 14 e 16 Ω cm) e di tipo «n» (di resistività uguale a circa 12 Ω cm). Le misure sono state effettuate in funzione dell'intensità del campo di induzione magnetica, fra 0.15 e 1.0 Wb/m², per varie orientazioni di questo rispetto alla corrente e agli assi cristallografici dei cristalli. È stato effettuato il confronto fra i risultati delle misure e le teorie esistenti, basate sulle attuali conoscenze sulla struttura delle bande di valenza e di conduzione del germanio. Per il germanio di tipo «p», il confronto con la teoria di Harman, Willardson e Beer (banda di valenza doppiamente degenere) è risultato solo in parte soddisfacente. Per il germanio di tipo «n», il confronto con la teoria Abeles e Meiboom (superfici di energia ellissoidali in prossimità dei minimi della banda di conduzione) è anch'esso soddisfacente e permette di stabilire che il valore del rapporto fra la massa efficace longitudinale degli elettroni di conduzione e quella trasversale deve essere nel germanio, a temperatura ambiente, inferiore a 15.6. I valori ottenuti per questo rapporto sono compresi fra 7 e 11.4; il valore più probabile è uguale a 8.3.

A. DE MARCO. Vedi pag. 433.

L. DE MARCO e A. DRIGO (Ferrara). — Effetto di un campo elettrico sulla polimerizzazione di alcune sostanze, e conseguenti modificazioni di talune costanti fisiche.

Monomeri polari come il nitrile acrilico, il metil-metaacrilato, ecc. si sono fatti polimerizzare a temperature convenienti, in presenza di un campo elettrico di circa 3000 V/cm. Il processo di polimerizzazione è stato seguito nelle sue varie fasi confrontandolo con quello caratteristico delle medesime sostanze polimerizzate alla stessa temperatura in assenza di campo elettrico. Gli effetti del campo elettrico sulle qualità dei polimeri ottenuti sono stati infine esaminati procedendo allo studio di talune costanti fisiche.

F. DEMICHELIS (Torino). — Spettrometri magnetico e a scintillazione per raggi γ . Caso del $^{228}_{90}\text{Th}$ e suoi prodotti di decadimento.

Si dispone attualmente di una spettroscopia per particelle emesse da sostanze radioattive, in particolare per raggi γ , fondata su due metodi: 1) spettrometro magnetico; 2) spettrometro a scintillazione. Lo spettro γ del $^{212}_{84}\text{Po}$ è notevolmente complesso e ha fatto oggetto di studio allo spettrometro magnetico da parte di molti autori. I risultati, non del tutto concordi, vengono confrontati con quelli ottenuti con uno spettrometro a scintillazione.

E. DI CAPUA. Vedi pag. 433.

A. DRIGO e M. PIZZO (Ferrara). — Comportamento di materiali ferromagnetici a cristalli orientati in alcuni fenomeni magnetici e magnetoelastici.

Lamierini di Fe-Si trattati col procedimento derivato dalle ricerche di Goss sono stati esaminati per mettere in rapporto con la loro direzione di maggiore permeabilità le direzioni di anisotropia magnetica, le modalità con cui si compiono le discontinuità di Barkhausen, la resistenza elettrica e le variazioni di questa conseguenti a magnetizzazione con campi formanti angoli opportuni rispetto alla direzione di preferenziale orientazione dei granuli. Con un metodo dinamico è stato pure misurato il modulo elastico in diverse direzioni, e le sue variazioni conseguenti a magnetizzazione lungo le direzioni medesime. Le vibrazioni indotte nei campioni erano di tipo flessionale o estensionale, nel vuoto: in entrambi i casi si è cercato di stabilire anche come si modifica la dissipazione interna in conseguenza della magnetizzazione.

A. DRIGO. Vedi pag. 447.

U. FACCHINI, M. FORTE, A. MALVICINI e T. ROSSINI (Milano). — Nuovi tipi di camere di ionizzazione per la misura di spettri e loro utilizzazione per l'esame di minerali di uranio e torio.

L'utilizzazione delle camere di ionizzazione a griglia per lo studio degli spettri α è molto semplificata con l'uso di una miscela di argon e azoto. Con questa miscela è possibile vuotare e riempire la camera nel giro di poche decine di secondi. Vengono descritti alcuni nuovi tipi di camere di ionizzazione di cui una è a flusso di gas e il campione emettitore α viene introdotto per mezzo di una slitta. L'introduzione del campione non altera il funzionamento della camera, che è subito pronta per il rilievo dello spettro α . La seconda è a pressione e permette una migliore risoluzione in tempo (2 μ s) ed in energia (larghezza di riga 2%). Una terza è per grandi superfici emittenti e permette lo studio di attività molto basse. Queste camere vengono usate per l'analisi di minerali radioattivi. Un piccolo campione di minerale dell'ordine di 10 mg viene macinato e steso in forma di strato sottile su un disco di alluminio. Lo studio dello spettro energetico delle particelle α permette di individuare i vari nuclidi emittitori. Con questo metodo è possibile distinguere minerali di uranio da minerali di torio e fare un'analisi quantitativa; è possibile anche stabilire il grado di equilibrio radioattivo e le fughe di emanazione dai minerali. Vengono presentati risultati con minerali contenenti quantità dell'ordine di 10^{-3} di uranio e di torio e viene descritta una nuova apparecchiatura per condurre questo tipo di analisi fino ad attività corrispondenti a concentrazioni dell'ordine di 10^{-5} .

U. FASOLI, C. MARONI, I. MODENA, E. POHL e J. POHL-RÜLING (Padova). — Determinazione sperimentale dei coefficienti di correlazione delle intensità dei mesoni μ di due segni nella radiazione cosmica al livello del mare con la pressione atmosferica e l'altezza dello strato di 100 Mb e interpretazione dei risultati.

Con un dispositivo di contatori Geiger sono state misurate le intensità verticali dei mesoni μ^+ , μ^- discriminati in segno da un lampo magnetico. Le intensità medie registrate sono di 5600 μ^+ e 4620 μ^- al giorno e il periodo di misure è di

18 mesi. Si sono ricavati i coefficienti di correlazione delle intensità dei μ^+ , μ^- con la pressione atmosferica al livello del mare (α^+ e α^-) e con l'altezza dello strato di 100 Mb (γ^+ e γ^-). I coefficienti trovati sono diversi per i mesoni dei due segni, al di fuori degli errori statistici e precisamente $|\alpha^-| > |\alpha^+|$ e $|\gamma^+| > |\gamma^-|$. I risultati ottenuti sono stati interpretati mediante un particolare integrale dell'equazione di diffusione e considerando i mesoni come prodotti da due sorgenti distinte: una costituita dagli urti della primaria con i nuclei dell'alta atmosfera e l'altra dagli urti della nucleonica secondaria.

M. FENOGLIO (Torino). — Relazioni cristallografico-strutturali tra il difenile e i suoi nuovi derivati.

Oggetto della presente comunicazione sono i risultati più notevoli sinora ottenuti nello studio cristallografico-strutturale di un gruppo di nuovi derivati del difenile, in parte nitroderivati ed in parte cloroaminoderivati. Tanto i reperti relativi alle proprietà morfologiche che a quelle fisiche — ed in particolare alle proprietà ottiche — hanno consentito di istituire interessanti raffronti con le corrispondenti del composto capostipite: il difenile. Per quanto riguarda le proprietà ottiche, viene discusso il ruolo notevolmente importante da esse assunto nel determinare forma e orientazione dei leptoni. I risultati dell'indagine röntgenografica hanno permesso non solo di controllare la simmetria e le costanti cristallografiche determinate per via goniometrica dei nuovi derivati del difenile, ma hanno altresì fornito gli elementi indispensabili per la determinazione della struttura degli stessi, che viene discussa e messa in relazione con la struttura del difenile. Il calcolo del numero di molecole Z , contenute nella cella elementare, applicando la nota relazione: $Z = V_0 \rho N / M$ in cui normalmente sono determinati per via sperimentale le costanti reticolari, che consentono di calcolare V_0 , il peso specifico ρ ed il peso molecolare M , offre occasione di mettere in evidenza il ruolo importante assunto da N , numero di Avogadro, in strutturistica.

F. FERRARI. Vedi pag. 445.

F. FERRERO, L. GONELLA, R. MALVANO, C. TRIBUNO and O. HANSON (Torino). — Fast Neutron Component in Photoneutron Reaction.

The integrated cross sections for fast neutrons from photonuclear reactions are observed in several (43) elements with (n, p) threshold detectors. These integrated cross sections (normalized to the sum rule factor NZ/A) seem to be rather constant throughout the entire table of elements, rising however significantly in the neighborhood of the neutron numbers 50, 82, 126. For light elements this regularity, however, is less evident. For some elements (Cu, Ba, Bi, Au.) the excitation function and the angular distribution for fast neutrons have been observed with the same detectors. The experimental angular distribution of the fast neutron component can be represented by a function of the type $1 + a \sin^2 \vartheta + b \cos \vartheta$, where b , which describes a small forward component, is very much smaller than a . The excitation function indicates that the fast neutrons are produced predominantly by photons in the region of the giant resonance, giving further experimental evidence that the giant resonance can be attributed to strong individual particle transition rather than a collective type of photon absorption resulting in a

general nuclear heating. The excitation function indicates however that a small fraction of fast neutrons are produced outside of the giant resonance by a somewhat different direct process. The above experimental data are finally discussed in the framework of the single particle model of the photonuclear reactions, obtaining in certain cases a rather good agreement with theory.

L. FERRETTI. Vedi pag. 437.

A. FERRO e G. MONTALENTI (Torino). — Sulle variazioni delle proprietà magnetiche ed elastiche causate dall'idrogeno disciolto nel ferro.

Si riassumono criticamente le leggi fondamentali che regolano la soluzione dei gas biatomici nei metalli: in particolare il comportamento dell'idrogeno nel ferro. Si dà un'interpretazione degli effetti meccanici e magnetici causati dai gas che si disciolgono nei metalli con processo endotermico, cioè nei casi nei quali non si forma composto chimico definito tra gas e metallo. Si dimostra che, per spiegare i fatti, è necessario ammettere che il gas contenuto nel metallo allo stato atomico tenda a precipitare in molecola biatomica entro cavità ellittiche dell'ordine di grandezza di alcune decine di diametri atomici determinando nell'interno della microcavità una forte pressione; questa forte pressione nei materiali duri può produrre la rottura spontanea, nei materiali dolci la formazione di cavità in forma di bollicine visibili ad occhio nudo ed una notevole deformazione plastica che determina a sua volta un aumento del campo coercitivo di saturazione. Si riferisce su esperienze eseguite su ferro caricato con idrogeno a paragone con ferro deformato plasticamente. L'andamento del campo coercitivo di saturazione, misurato a temperatura ambiente, in funzione della temperatura di ricottura è identico nei due casi. Pertanto le ipotesi poste alla base della spiegazione dei fatti su accennati hanno conferma sperimentale. Da considerazioni tratte dalla teoria della precipitazione si stima la distanza media dei centri di precipitazione dell'idrogeno ottenendo valori di circa $2 \cdot 10^{-3}$ cm in buon accordo coi dati sperimentali.

A. FERRO e G. MONTALENTI (Torino). — Sul rilassamento meccanico e magnetico ad elevata temperatura in ferro puro e leghe di ferro.

Nel presente lavoro si studia l'attrito interno meccanico ed il corrispondente rilassamento magnetico (variazione di permeabilità iniziale in seguito a smagnetizzazione) su diversi materiali (nichel; lega di ferro al 40% di nichel; ferro dolce; ferro silicio al 4%; ferro silicio all'1%) in funzione della temperatura, con particolare riguardo a quanto accade a temperature notevolmente superiori a quella dell'ambiente. Le misure di attrito interno sono eseguite mediante pendolo di Kê. La valutazione dell'entità del rilassamento magnetico è eseguita misurando il decremento di permeabilità iniziale (misurata in corrente alternata a circa 30 Hz) che si osserva nei primi 15 minuti dalla smagnetizzazione. Le conclusioni generali che si possono trarre dalle esperienze eseguite sono le seguenti. In tutti i materiali esaminati si osserva che a temperatura elevata il rilassamento magnetico presenta un massimo che cade molto prima che sia raggiunta la temperatura di Curie. La curva del rilassamento meccanico in funzione della temperatura presenta o un massimo o un flesso per poi salire

rapidamente al crescere della temperatura. Si può pertanto ammettere, come ragionevole ipotesi di lavoro, che il rilassamento meccanico osservato a temperatura elevata sia dovuto a due cause distinte: l'una che determina «soltanto» rilassamento meccanico, l'altra che determina «anche» rilassamento magnetico. Allo stato attuale dei fatti non è possibile fare ipotesi più specifiche. Occorrerebbe ad esempio sperimentare su monocristalli di ferro e su campioni di ferro fortemente poligonizzato per decidere l'influenza, su questi fenomeni, delle dislocazioni e del rilassamento al bordo dei grani.

Nel ferro puro e nella lega di ferro al 40% di nichel l'energia di attivazione dei fenomeni di rilassamento osservati a temperature elevate sono notevolmente più alte di quelle caratteristiche della diffusione interstiziale degli atomi di carbonio ed azoto e precisamente dell'ordine di 70000 ± 80000 cal/mole. Anche la curva che rappresenta l'entità del rilassamento magnetico in funzione dell'intensità del campo di misura è diversa: in luogo di presentare un massimo nell'intorno di 2 Asp/m rimane praticamente costante fino a 60 Asp/m. Nel ferro silicio invece le costanti di tempo sono quelle caratteristiche della diffusione interstiziale così come l'andamento della curva dell'intensità del rilassamento magnetico in funzione dell'intensità del campo di misura. Sembra pertanto lecito ammettere che l'intensissimo rilassamento magnetico e meccanico sia dovuto alla diffusione di atomi di silicio che si dovrebbero trovare nel reticolo del ferro in posizione interstiziale.

G. FIDECARO, J. M. CASSELS, A. WETHERELL and J. R. WORMAND (*Liverpool*).
 - **On the Reaction $\pi^- + p$.**

A total absorption γ -ray spectrometer has been used to determine the ratio of the probabilities of the two following reactions, when negative pions are stopped in Hydrogen: $\pi^- + p \rightarrow n + \pi^0 \rightarrow n + 2\gamma$, $\pi^- + p \rightarrow n + \gamma$. The spectrometer has been calibrated with monoenergetic electrons and positrons obtained from the electron contamination of the 95 MeV negative pion beam. The numerical value for the ratio of the probabilities, obtained in this experiment is more consistent with the accepted interpretation of the low energy pion-proton scattering and the photoproduction, than the previous value measured by PANOFSKY *et al.* This experiment has been done with the 380 MeV synchrocyclotron of the Nuclear Physics Research Laboratory at the University of Liverpool.

E. FIORINI, R. GIACCONI, A. SICHIROLLO e C. SUCCI (*Milano*). - **Una camera di Wilson di grandissime dimensioni.**

Nella presente relazione viene descritta una camera di Wilson di volume utile $126 \times 116 \times 50$ cm³, adatta a contenere fino a $20 \div 25$ piastre di materiale condensato. L'espansione della camera è ottenuta mediante il movimento di una membrana rinforzata; per compiere l'operazione con sufficiente rapidità si è utilizzato un sistema a due stadi in cascata, di cui il primo pilotato da una valvola del tipo di Fussell a controcampo. Il rapporto di espansione è regolato a pressione. Un dispositivo di comando, a grande flessibilità, compie tutte le operazioni del ciclo, parte meccanicamente e parte elettronicamente. Per l'illuminazione vengono impiegate quattro lampade a flash, da circa 10000 joule ciascuna, dotate di specchi parabolici ed alimentate da una batteria di condensatori da 5000 μ F, caricata a 4500 V.

S. FOCARDI. Vedi pag. 435.

L. FONDA and I. REINA (*Trieste*). — **Nucleon Recoil in the Pion-Nucleon Scattering.**

The effect of nucleon recoil has been taken into account in the extended source theory of pion-nucleon scattering with PS-PV interaction Hamiltonian. The comparison of the results on *P*-wave with experimental data and with the results of Chew's cut-off theory has been carried out. The influence of nucleon recoil in the determination of the renormalized coupling constant has been discussed. In order to discuss, on the same theoretical line, the influence of nucleon recoil on *S*-phases, two terms, bilinear in the meson field, have been added to the PS-PV coupling as can be obtained from a Dyson-Foldy transformation applied to the PS-PV interaction Hamiltonian. The effect of nucleon recoil has been found to be large.

M. FORTE. Vedi pag. 448.

C. FRANZINETTI. Vedi pag. 441.

I. GABRIELLI e G. IERNETTI (*Trieste*). — **Campi ultrasonori stazionari e processi in sistemi eterofasi.**

Il processo di adsorbimento di iodio in soluzione acquosa diluita, da parte dell'amido, è stato utilizzato da G. S. BENNETT ⁽¹⁾ per registrare sezioni normali di fasci ultrasonori, mediante colorazione localizzata di strati d'amido, distesi su lastre di vetro. Si è affinata la tecnica di Bennett, usandola sia come sensibile metodo di ultrasonografia, sia per studiare l'influenza dei parametri del campo ultrasonoro sul processo suddetto. Si sono impiegati campi stazionari realizzati secondo una disposizione precedentemente discussa ⁽²⁾, la quale permette il costante controllo meccanico della densità di energia e delle condizioni di risonanza della colonna liquida. Le registrazioni delle sezioni longitudinali risultano rigate più o meno regolarmente in corrispondenza delle mezze lunghezze d'onda, mostrando come la struttura del campo dipende dalle condizioni di risonanza. L'amido si colora in corrispondenza dei ventri di pressione. È stata misurata la dipendenza della colorazione delle lastre, registranti sezioni normali del fascio, dalla frequenza degli ultrasuoni (da 0.4 a 4 MHz), dalla densità di energia (fino a 200 J/m³) e dal tempo di irraggiamento. Al di sotto della soglia di cavitazione di degassamento l'opacità delle lastre aumenta circa linearmente con la densità di energia e col tempo e diminuisce lievemente al crescere della frequenza. La cavitazione comporta un aumento dell'opacità tanto maggiore quanto più bassa è la frequenza nell'intervallo considerato. Si è potuta mettere in evidenza l'importanza di alcuni meccanismi: pressione alternativa, cavitazione, moto convettivo idrodinamico dovuto a varie cause, nella cinetica dei processi in sistemi liquido-solido.

⁽¹⁾ G. S. BENNETT: *Journ. Acoust. Soc. Am.*, **24**, 470 (1952).

⁽²⁾ I. GABRIELLI e G. IERNETTI: *Suppl. Nuovo Cimento*, **4**, 1067 (1956).

F. GAETA. Vedi pag. 439.

C. M. GARELLI. Vedi pag. 446.

R. GESSAROLI. Vedi pag. 437.

G. GIACCONI. Vedi pag. 451.

S. GIAMBUZZI, C. MARCHI, G. QUARENI e A. WATAGHIN (*Bologna*), G. LUGARINI, S. MORA e G. DASCOLA (*Parma*). - **Scattering elastico** $\pi^+ + P$ a 178 MeV.

Un pacco di emulsioni fotografiche è stato esposto al fascio di particelle positive (320 MeV/c) prodotte col cosmotrone di Brookhaven. Mediante osservazione per traccia sono stati trovati 246 eventi $\pi^+ + P$. L'energia dei π^+ interagenti è stata determinata in base all'angolo di scattering e al range del protone di rinculo. È stata riscontrata una notevole dispersione nell'energia del fascio d'entrata (da 150 a 270 MeV). Le energie di interazione si distribuiscono però intorno al valore medio 178 MeV, con dispersione di ± 25 MeV. Il valore medio 178 MeV risultante dall'analisi di 111 eventi è stato determinato con scarto quadratico medio 2 MeV. La distribuzione angolare trovata si può rappresentare con la seguente espressione:

$$D(\theta) = \frac{\sigma(\theta)}{\sigma_T} = \frac{a + b \cos \theta + c \cos^2 \theta}{\sigma_T}$$

Considerando l'andamento con l'energia dei coefficienti a/σ_T , b/σ_T , c/σ_T ottenuti in altri esperimenti finora eseguiti si può mostrare che i valori medi di a/σ_T , b/σ_T , c/σ_T , in un largo intervallo intorno all'energia di risonanza, coincidono con grande approssimazione con i valori da attendersi per l'energia media. Normalizzando la distribuzione angolare trovata alla sezione di urto totale, $\sigma_T = 200$ mb, più attendibile per l'energia di 178 MeV, la sezione d'urto differenziale risulta:

$$\sigma(\theta) = (6.87 - 1.36 \cos \theta + 41.76 \cos^2 \theta) \text{ mb/sr}.$$

L'analisi ha dato due possibili gruppi di fasi (tipo Fermi):

$$\begin{array}{lll} \alpha_3 = -9.1^\circ & \alpha_{33} = 76.0^\circ & \alpha_{31} = 11.4^\circ \\ \alpha_3 = -18.6^\circ & \alpha_{33} = 71.7^\circ & \alpha_{31} = 12.1^\circ \end{array}$$

L. GONELLA. Vedi pag. 449.

K. GOTTSTEIN. Vedi pag. 436, 437.

O. GOUSSU. Vedi pag. 431.

W. D. B. GREENING. Vedi pag. 444, 464.

A. GRIECO. Vedi pag. 440.

M. GRILLI. Vedi pag. 432.

E. GROSSETTI (Napoli). — Rotazione di liquidi polari in campo elettrico rotante.

Il DEBYE come ben noto, ha previsto la genesi di un momento meccanico quando un dielettrico dipolare liquido è posto in campo elettrico rotante. La verifica di questo effetto per numerosi liquidi e per varie frequenze è stata effettuata da LAERTES. Noi abbiamo iniziato nuove misure in questo campo, dato che tale metodo permette una diversa determinazione del coefficiente d'attrito interno dei liquidi, noto il momento dipolare. Le misure sono state condotte in questo primo momento per frequenze bassissime (50 Hz). Per ora si può affermare che per i liquidi quali l'acqua ed il toluolo, pur tenendo conto della conducibilità della prima, il rapporto dei due momenti meccanici è molto diverso dal rapporto dei due momenti dipolari. È necessario però tener conto dell'effetto notevole dovuto all'isteresi dielettrica del recipiente, e all'azione del velo d'umidità, e cioè dell'azione di strati di dipoli presumibilmente orientati.

L. GUERRIERO. Vedi pag. 432, 444.

O. HANSON. Vedi pag. 449.

G. IERNETTI. Vedi pag. 452.

S. JANNELLI e F. MEZZANARES (Messina). — Caratteristiche delle disintegrazioni prodotte da protoni negli elementi pesanti delle emulsioni nucleari.

Si espongono i risultati dell'analisi di 854 stelle prodotte da protoni di $140 \pm \pm 6$ MeV in emulsioni nucleari Ilford G5. Risultati preliminari, relativi essenzialmente alle sezioni d'urto, furono già comunicati al Congresso di Pisa (Gingno 1955). Nel presente lavoro si svolge un'analisi dettagliata delle caratteristiche delle stelle, con particolare riguardo a quelle prodotte negli elementi pesanti dell'emulsione (Ag e Br) e distinguendo tra esse le stelle dotate di rinculo visibile. Si studiano le distribuzioni angolari dei protoni di alta energia (tracce « grige »; $T > 30$ MeV), dei protoni di bassa energia e delle particelle α e si confrontano i risultati con quelli ottenuti da altri autori e con quelli deducibili dallo studio teorico delle due fasi della produzione delle stelle: la cascata nucleonica e la successiva evaporazione nucleare. Analogamente si studia — e si analizza con particolare attenzione — lo spettro energetico delle particelle di bassa energia. I dati ottenuti mentre risultano generalmente in buon accordo con quelli già noti, presentano una migliore validità dal punto di vista statistico, dato l'elevato numero degli eventi analizzati.

L. JESS. Vedi pag. 455.

D. KEEFE. Vedi pag. 431.

A. KERNAN. Vedi pag. 431.

A. KIND e L. JESS (Padova). – Sulla parte reale del potenziale complesso del nucleo.

A partire da una interazione nucleone-nucleone che soddisfa i dati sperimentali relativi ai sistemi di due nucleoni per basse energie, si è determinata la parte reale centrale V del potenziale complesso del nucleo, valevole per le interazioni neutrone-nucleo e protone-nucleo, sia per un nucleone legato, che per un nucleone incidente con energia compresa tra 0 e 400 MeV. L'approssimazione usata è quella che esclude correlazioni tra nucleoni nel nucleo. Il carattere di scambio dell'interazione nucleone-nucleone risulta essere essenziale nella determinazione di V . Si fa un'analisi della relazione tra risultati teorici e dati sperimentali.

E. LAZZARINI. Vedi pag. 435.

L. LENDINARA. Vedi pag. 437.

F. LEPRI. Vedi pag. 430.

R. LEVI SETTI. Vedi pag. 431.

S. LIMENTANI. Vedi pag. 464.

A. M. LIQUORI (Roma). – Su alcune questioni riguardanti angoli e distanze di legame nelle molecole organiche.

Sulla base di risultati ottenuti nella determinazione di angoli e distanze di legame in eterocicli azotati mediante diffrazione dei raggi X sono state stabilite alcune relazioni fra struttura molecolare ed elettronica che possono venire utilmente impiegate nel delucidare le proprietà fisiche e chimiche di questa importante classe di molecole.

A. LORIA. Vedi pag. 444.

J. LOSTY. Vedi pag. 431.

A. LOVATI. Vedi pag. 444.

G. LUGARINI. Vedi pag. 453.

R. MALVANO. Vedi pag. 449.

A. MALVICINI. Vedi pag. 448.

W. MANCINI. Vedi pag. 440.

A. MANFREDINI. Vedi pag. 441.

C. MARCHI. Vedi pag. 453.

F. MARIANI (Roma). — Sulla correlazione tra attività solare e densità elettronica ionosferica.

Da un esame comparato degli andamenti dei valori mediani mensili di densità elettronica massima N negli strati ionosferici, estesa a circa 20 Osservatori distribuiti tra le latitudini di 43° Sud e 50° Nord per il periodo 1948-1954 (fare decrescente del cielo solare) si traggono taluni interessanti risultati: *a)* La relazione tra gli andamenti a lungo termine di N e del numero R di Wolf, usualmente considerata lineare secondo la relazione: (1) $N \propto 1 + \alpha R$, appare meglio approssimata da una relazione del tipo (2) $N \propto 1 + \beta R + \gamma A$, ove A indica un altro parametro legato all'attività solare che sembra possa identificarsi con l'area A_F dei filamenti di idrogeno osservati sul disco solare. *b)* Usando la (1) i valori di α appaiono sensibilmente più grandi nell'emisfero Nord che nell'emisfero Sud, tanto più quanto più cresce la latitudine Nord. Assumendo invece la (2) si ottengono valori di β sensibilmente uguali nei due emisferi mentre l'asimmetria, sempre nello stesso senso, si trasferisce ai coefficienti γ . *c)* Isolando la componente N_{12} di densità elettronica di periodo 12 mesi e studiando le correlazioni tra le successioni dei valori mensili di $N - N_{12}$ e dei valori mensili di R e di A_F , si ottengono ancora risultati in favore di una differente dipendenza di $N - N_{12}$ dall'area dei filamenti di idrogeno, con modalità del tutto analoghe a quelle della correlazione e tra gli andamenti a lungo termine. In conclusione sembra di poter affermare la presenza di qualche causa ionizzante interessante maggiormente o essenzialmente l'emisfero Nord, poco o affatto correlata con il numero di Wolf; le ipotesi che si possono fare per spiegare i fatti riscontrati sono, allo stato attuale, quasi soltanto speculative.

F. MARIANI (Roma). — Sulle oscillazioni di marea nell'atmosfera.

Come è noto, le oscillazioni di marea nell'atmosfera sono attribuite a un fenomeno di risonanza dell'atmosfera stessa, indotto dal Sole e, in minore misura, dalla Luna. Tenuto conto di questo fatto ed estendendosi le oscillazioni fino alle regioni ionosferiche, appare interessante studiare l'effetto provocato dalla considerazione della variabilità con la quota della accelerazione di gravità g , la quale in tutte le trattazioni finora date viene assunta costante. Dai primi risultati parziali, ottenuti per un modello di atmosfera a « scala delle altezze » costante con la quota, appare evidente che, per la forma stessa della soluzione delle equazioni che governano le oscillazioni di marea, possono aversi differenze non trascurabili tra le ampiezze delle oscillazioni di pressione nei due casi g variabile e g costante e differenze forse maggiori sul livello a cui tali oscillazioni cambiano di fase.

C. MARONI. Vedi pag. 448.

M. MERLIN. Vedi pag. 432, 464.

F. MEZZANARES. Vedi pag. 451.

A. MICHELINI. Vedi pag. 433.

C. MILONE (Catania). — Fotoprotoni dall'ossigeno.

Esponendo direttamente ai raggi γ di energia massima 30 MeV del Betatrone B.B.C. di Torino, lastre nucleari secche ed imbevute di H_2O nel rapporto di circa 3 g di H_2O per cm^3 di emulsione secca, si è trovato nelle emulsioni imbevute un numero di tracce di protoni circa 3 volte maggiore che nelle emulsioni secche, a parità di esposizione. Misure eseguite con lastre imbevute di D_2O danno, entro il 10%, lo stesso numero di tracce che le misure eseguite con lastre imbevute di H_2O . Si deduce che circa il 70% delle tracce di protoni osservate nelle emulsioni imbevute di acqua è attribuibile a processi di fotoemissione in ossigeno. La sezione d'urto per fotodisintegrazione integrata fino a 30 MeV risulta in ossigeno alcune volte maggiore della sezione d'urto dello stesso O integrata fino a 20 MeV. Ciò mostra che nell'ossigeno oltre alla risonanza γ, p con picco a 15 MeV messa in evidenza da SPICER esiste anche una più elevata risonanza γ, p per gamma d'energia maggiore di 20 MeV; risonanza che non è stata ancora messa in evidenza. Lo spettro energetico dei protoni osservati risulta di più molle di quello che ci si attenderebbe in base al valore della soglia e all'andamento della sezione d'urto in corrispondenza della risonanza gigante, nell'ipotesi di un processo diretto.

C. MILONE, R. RICAMO, R. RINZIVILLO e A. RUBBINO (Catania). — Fotoeffetto nucleare nell'ossigeno e nell'alluminio con raggi gamma polarizzati.

È stata studiata la distribuzione azimutale dei fotoprotoni emessi dall'ossigeno e dall'alluminio irradiati con raggi γ del Betatrone B.B.C. da 30 MeV di Torino. Adoperando una camera a pressione ridotta e in condizioni sperimentali analoghe a quelle impiegate per lo studio dei fotoprotoni dal carbonio è stata osservata, in Lastre Ilford C2 di 200 μm , la distribuzione azimutale dei protoni emessi dall'alluminio. Quelli aventi in emulsione un percorso inferiore a 200 μm presentano una distribuzione con un marcato massimo a $\varphi = 35^\circ$ e 75° . I protoni aventi in emulsione un percorso superiore a 200 μm , cioè energia superiore a 5.5 MeV, hanno una distribuzione azimutale con due decisi massimi per $\varphi = 10^\circ$ e 65° . Analoghe misure sulla distribuzione azimutale sono state eseguite con un'altra tecnica sperimentale consistente nell'esporre direttamente ai raggi γ del betatrone le lastre coperte con Al di 0.5 mm di spessore adagiato sulla emulsione, ed esaminando nella emulsione la distribuzione delle tracce dei protoni provenienti dall'alluminio stesso. La distribuzione azimutale che si riscontra per le tracce aventi θ compreso fra 45° e 90° alla distribuzione che si riscontra nel caso delle misure con la camera. Si può così escludere che i massimi siano da attribuire ad errori sperimentali sistematici inerenti alla tecnica particolare impiegata. Per controllare che nel caso dell'esposizione con camera le anisotropie azimutali non fossero dovute ad errori di centraggio o comunque ad effetti spuri, lo scatterer di alluminio è stato esposto ai raggi γ emessi nella direzione dell'asse del fascio della Bremsstrahlung cioè a $\theta_\gamma = 0$. I protoni così rivelati mostrano una distribuzione isotropa entro gli errori statistici. Lo spettro energetico dei fotoprotoni emessi dall'Al è molto più molle di quello che ci sarebbe da attendersi in base alla soglia ed all'andamento della sezione d'urto, nell'ipotesi di un processo diretto, ma ciò probabilmente è anche dovuto al notevole spessore (0.5 mm) che si è dovuto dare all'alluminio per poter mettere in evidenza gli effetti di polarizzazione con modiche esposizioni. Lastre Ilford C2 secche ed imbevute di H_2O sono state inoltre esposte direttamente ai raggi γ polarizzati.

I fotoprotoni emessi dall'ossigeno, ottenuti per differenza tra i protoni nelle due diverse esposizioni, mostrano una distribuzione azimutale con andamento medio del tipo $I = a + b \sin^2 \varphi$. A questa si sovrappone però una modulazione con massimo intorno a 25° . La complessità della distribuzione angolare dei fotoprotoni da radiazione γ polarizzata osservati per l'alluminio e l'ossigeno, oltre che per il carbonio, sembra quindi essere un fatto generale di cui però appare per ora difficile una interpretazione teorica.

M. MILONE e E. BORELLO (Torino). — Sulla struttura della gliossima allo stato solido.

Si riferisce sui primi risultati ottenuti mediante l'analisi roentgenografica e la spettroscopia nell'infrarosso. Dall'esame degli spettri infrarossi allo stato solido risulta che le molecole della gliossima sono centrosimmetriche e piane ed appartengono al gruppo spaziale C_{2h} inoltre le molecole sono associate per la presenza di forti legami idrogeno. Lo studio roentgenografico ha permesso di stabilire che i cristalli appartengono al sistema monoclinico ed hanno le seguenti costanti cristallografiche:

$$\alpha = \gamma = 90^\circ \quad \beta = 88^\circ 30' \quad a = 3.88 \text{ \AA} \quad b = 4.45 \text{ \AA} \quad c = 11.08 \text{ \AA}$$

La cella elementare contiene 2 molecole. L'esame statistico sistematico delle riflessioni permette di scegliere il gruppo spaziale con certezza: C_{2h}^5 . In tale gruppo spaziale le coordinate delle posizioni equivalenti sono:

$$\bar{X}, Y, Z \quad \bar{X}, \bar{Y}, \bar{Z} \quad \bar{X}, \frac{1}{2} + Y, \frac{1}{2} - \frac{1}{2} - Z \quad X, \frac{1}{2} - Y, \frac{1}{2} + Z.$$

Poichè nella cella elementare le molecole sono due, ciascuna di esse dovrà occupare due posizioni equivalenti: la molecola deve essere pertanto centrosimmetrica. Il piano (100) è un piano di facile sfaldatura e poichè le molecole sono piane con ogni probabilità giaceranno sul piano YZ. Abbiamo esaminato in luce infrarossa polarizzata delle sottili lamine cristalline tagliate parallelamente al piano YZ. Le bande d'assorbimento corrispondenti alle vibrazioni di valenza dell'ossidrile e del C=N presentano dicroismo parallelo all'asse cristallografico b , mentre le vibrazioni di valenza del legame N—O di dicroismo perpendicolare. Con ogni probabilità quindi il legame C—C della gliossima è di poco inclinato rispetto all'asse c e le molecole formano lunghe catene parallelamente all'asse b per mezzo dei legami idrogeno. Ciò è confermato dal fatto che i piani (001) sono anch'essi piani di facile sfaldatura.

A. MINGUZZI (Bologna). — Interazione di fotoni con un campo elettromagnetico costante.

Dato un campo elettromagnetico costante caratterizzato da $\mathbf{H} \cdot \mathbf{E} = 0, H^2 - E^2 > 0$, si è studiata la corrente di polarizzazione del vuoto generata dalla sovrapposizione di tale campo con un campo elettromagnetico «debole» comunque, variabile. Si sono considerati i termini di corrente dipendenti linearmente dal campo «debole» ma non si è ricorso a uno sviluppo in serie nel campo costante. Si può dapprima scegliere come riferimento quello in cui il campo costante si riduce a un campo magnetico costante parallelo all'asse zeta, h . Dopo rinormalizzazione della carica elettrica la cor-

rente del vuoto si può esprimere come sovrapposizione di un termine dipendente dalla corrente generante il campo « debole » $J_{\mu}^{est}(x)$, più termini che dipendono dalle derivate del campo « debole ». Si possono scrivere immediatamente le equazioni di Maxwell a cui obbedisce il campo « debole », aggiungendo alla sorgente del campo la corrente di polarizzazione del vuoto. Nel caso fisicamente interessante in cui la sorgente $J_{\mu}^{est} = 0$, le equazioni di Maxwell si possono integrare facilmente; la conclusione fisica è che la regione in cui esiste il campo costante si comporta come un dielettrico anisotropo; per esempio un'onda elettromagnetica piana che entra normalmente al campo magnetico e il cui vettore elettrico forma un angolo $\alpha \neq 0.90^\circ$ col campo magnetico esce dalla regione del campo magnetico polarizzata ellitticamente. E ciò perchè analogamente a quello che avviene in un cristallo monoassico, l'indice di rifrazione dalla imponente polarizzata parallelamente al campo magnetico è diverso dall'indice di rifrazione della componente polarizzata normalmente al campo magnetico. Naturalmente tali indici di rifrazione dipendono fortemente anche dalla frequenza dell'onda. Tali indici di rifrazione però non si possono esprimere in forma chiusa nel campo magnetico e nella frequenza. Gli integrali che ci esprimono la dipendenza dal campo magnetico, ci hanno permesso di concludere che tali indici di rifrazione non sono funzioni analitiche nel punto $h = 0$ del campo magnetico; le serie ottenute sviluppando attorno ad $h = 0$ gli integrali è divergente, ma però tale serie converge asintoticamente per $h \rightarrow 0$.

I. MODENA. Vedi pag. 848.

G. MONETTI. Vedi pag. 433.

G. MONTALENTI. Vedi pag. 450.

S. MORA. Vedi pag. 453.

M. PANETTI. Vedi pag. 444.

G. PATERGNANI. Vedi pag. 443.

L. PELI. Vedi pag. 438.

M. PIERUCCI (*Modena*). — **Sull'età dell'universo.**

Cinque anni indietro l'A. riprendeva il concetto di « tempo assoluto » compatibile con la Relatività, introdotto già da POLVANI sotto forma di tempo entropico; faceva vedere come il tempo entropico coincida col tempo di espansione; e passava poi a calcolare, in questo tempo assoluto, l'età dell'universo. A questo proposito l'A. osservava come esistesse allora una grave discrepanza, messa già in evidenza dallo stesso EINSTEIN, fra età della Terra, dedotta dalle trasformazioni radioattive, ed età dell'universo, dedotta dall'espansione; in quanto che quest'ultimo tempo risultava minore del primo. Si proponeva quindi di togliere una tale discrepanza; e vi riusciva valendosi, in una prima approssimazione, degli invarianti della relatività ristretta, e valendosi poi di formule approssimate, ricavate dalla relatività generale. Il metodo, però, richie-

deva una ipotesi supplementare: quella della densità dell'universo all'inizio dell'espansione. Ciò rendeva il risultato assai malsicuro: si arrivava infatti, con varie ipotesi sulla densità iniziale, a valori assai diversi fra di loro, e tutti molto alti. L'A. riprende ora la questione, valendosi di una osservazione di natura astronomica, che permette di fare a meno della conoscenza della densità iniziale dell'universo, portando a modificare, nello stesso tempo, lo sviluppo pratico del metodo. È noto che l'espansione dell'universo può anche ricavarsi teoricamente (MILNE) trattando l'universo come un gas di particelle, che spontaneamente si diffonda. Ora le osservazioni astronomiche ci dicono che devesi parlare di un gas stellare dentro ogni ammasso di stelle, di un gas di ammassi stellari dentro ogni galassia, di un gas di galassie dentro ogni ammasso di galassie, di un gas di ammassi galattici dentro l'universo, tutti espandentisi contemporaneamente. Come rapporto fra densità iniziale ed attuale dell'universo basta mettere così, nel calcolo, il rapporto fra le densità medie (attuali) di due classi successive, nell'ordine segnato sopra. Si arriva in tal modo ad una età dell'universo di circa undici miliardi di anni; e si mostra infine come tale età, circa doppia di quella data recentemente per la Terra, ben si accordi con i recenti risultati dedotti dalle trasformazioni radioattive.

G. PISENT. Vedi pag. 43'.

M. PIZZO. Vedi pag. 448.

E. POHL. Vedi pag. 448.

J. POHL-RÜLING. 448.

F. PORRECA. Vedi pag. 440.

M. PUGLISI. Vedi pag. 430.

G. PUPPI. Vedi pag. 437, 442.

G. QUARENI. Vedi pag. 437, 442, 453.

I. F. QUERCIA. Vedi pag. 430.

L. A. RADICATI e S. ROSATI (*Pisa*). — Sul decadimento β del mesone K^0 .

Si studia lo spettro dell'elettrone e del pione emesso nel decadimento del mesone K^0 secondo lo schema $K^0 \rightarrow \pi + e + \nu$. Tale decadimento può considerarsi come una transizione β fra uno stato bosonico K^0 ed uno stato pionico. Si suppone per semplicità che l'interazione dipenda soltanto dall'impulso totale dell'elettrone e del neutrino escludendo cioè gli accoppiamenti con derivate di campi leptonici in analogia con quanto si conosce per il decadimento β . Lo spettro dipende dallo spin del mesone K^0 e dal particolare tipo di accoppiamento fra il mesone K^0 e il campo elettroneutrino. Ciò avviene anche per le «transizioni permesse» a differenza di quanto avviene per il decadimento β . Si studia pure la correlazione angolare fra l'elettrone e il pione emesso; anche essa fornisce indicazioni sullo spin del mesone K^0 .

A. RANZI. Vedi pag. 437.

I. REINA. Vedi pag. 452.

M. RENÉ. Vedi pag. 431.

J. REUSS. Vedi pag. 438.

D. REVEL. Vedi pag. 431.

R. RICAMO (*Catania*). - **Distribuzione azimutale dei fotoprotoni emessi dal carbonio e polarizzazione della bremsstrahlung.**

È stata studiata la distribuzione azimutale dei fotoprotoni emessi dal carbonio irradiato con i raggi γ del Betatrone B.B.C. da 30 MeV di Torino. Poichè i raggi γ della bremsstrahlung sono, come è noto, polarizzati, la distribuzione azimutale dei fotoprotoni può dare ulteriori informazioni circa i processi dell'effetto fotonucleare. I protoni sono stati rivelati mediante lastre Ilford C2 di 200 μm , di dimensioni 75 mm \times 75 mm esposte in una camera a pressione ridotta (qualche mm Hg) normalmente ai raggi γ collimati da un canale praticato in un blocco di Pb di 24 cm di spessore. L'asse z' del canale giaceva in un piano orizzontale (piano dell'orbita degli elettroni nel betatrone) e faceva un angolo $\theta_\gamma = \theta_0 = 1^\circ.5$ con la direzione z degli elettroni al momento dell'urto contro la targhetta del betatrone. L'angolo θ_0 è quello per cui c'è da aspettarsi un massimo nel valore della polarizzazione dei raggi γ della bremsstrahlung. La sezione del fascio di raggi γ nel piano dello scatterer era un cerchio di 12 mm di diametro, mentre lo scatterer era un disco di grafite di 5 mm di diametro e 0.5 mm di spessore. È stata curata fotograficamente la centratura dell'apparecchiatura in modo da evitare che il fascio di raggi γ potesse colpire le pareti della camera e del collimatore annesso a questa. È stata esaminata la corona circolare della lastra colpita soltanto dai protoni emessi con un angolo θ rispetto al fascio dei γ compreso tra 70° e 80° . La distribuzione azimutale dei fotoprotoni, assumendo come $\varphi = 0$ il piano contenente z e z' , risulta isotropa per i protoni che hanno in emulsione un percorso inferiore a 100 μm . I protoni aventi in emulsione un percorso superiore a 100 μm , cioè energia residua superiore a 3.6 MeV, hanno una distribuzione azimutale anisotropa con massimi per $\varphi = 15^\circ$ e 50° . Tali risultati sono stati ottenuti in diverse esposizioni al Betatrone distanziate nel tempo di mesi. Il totale delle tracce osservate ed accettate con lunghezza maggiore di 100 μm è di 3780. L'effetto osservato conferma che la bremsstrahlung è polarizzata e che la distribuzione azimutale dei protoni emessi è complessa, come già osservato da altri Autori per il deuterio con bremsstrahlung di energia massima inferiore a 22 MeV.

R. RICAMO. Vedi pag. 457.

G. RIGAULT (*Torino*). - **Relazioni tra la struttura della blenda e il contenuto in gallio e indio.**

In miei recenti studi sull'abbondanza e diffusione di gallio e indio in numerose blende appartenenti a giacimenti geneticamente differenti giunsi alla conclusione che non esiste parallelismo tra il contenuto di questi due costituenti minori

della blenda, nonostante la loro analogia di comportamento chimico. Allo scopo di spiegare questo fatto, ho ritenuto opportuno prendere in esame la struttura della blenda, poichè evidentemente soltanto con il considerare gli eventuali meccanismi di sostituzione di gallio e indio in rapporto alla struttura cristallina della blenda è possibile identificare le ragioni ultime del complesso fenomeno. Infatti sono riuscito a mettere in evidenza una notevole differenza tra i due tipi di meccanismi relativi alla sostituzione gallio-zinco e indio-zinco, in rapporto ai diversi raggi di coordinazione tetraedrica. È logico quindi cercare proprio in questa differenza la giustificazione del diverso comportamento di gallio e indio come costituenti minori nei confronti della blenda: infatti l'entità di una sostituzione isomorfa è funzione di vari fattori, tra cui il contributo all'energia reticolare portato dall'entrata di un elemento estraneo. Ora, a parità delle altre condizioni, se per i due costituenti minori questi valori di contributo all'energia reticolare sono differenti, ne viene di conseguenza che la temperatura di formazione in cui si hanno i massimi di concentrazione degli elementi vicarianti gallio e indio dovrà essere differente, senza parallelismo tra i loro tenori. Ho preso infine in considerazione la possibilità di trasformazioni nucleari per giustificare la presenza dell'indio nella blenda, possibilità che, in base ai risultati sperimentali a disposizione, non trovò conferma alcuna.

O. RIMONDI. Vedi pag. 438.

R. RINZIVILLO. Vedi pag. 457.

S. ROSATI. Vedi pag. 460.

T. ROSSINI. Vedi Vedi pag. 448.

Č. RUBBIA. Vedi pag. 435.

A. RUBBINO. Vedi pag. 457.

G. A. SALANDIN. Vedi pag. 432.

L. SCARSI. Vedi pag. 431.

M. SCHÖNBERG (*S. Paulo*). - **Quantum Kinematics and Geometry.**

A new kind of relations between quantum kinematics and ordinary geometry is discussed. It is shown that the Heisenberg (p,q) -algebra for a particle can be identified with a special kind of vector calculus of the affine three-dimensional space, by the introduction of a fundamental length. The algebras of the spins 0, $\frac{1}{2}$ and 1 are obtained from an extended form of the anticommutative Grassmann algebra of the space-time, which corresponds to a straightforward generalization of the ordinary vector calculus by the introduction of both contravariant and covariant vectors. An extension of the Grassmann algebra of points of the space-time gives the above generalized spin-algebra as well as the algebra of the isotopic spin of the nucleon,

which is thus associated to projective geometry. The geometric algebra associated to the Heisenberg (p, q) -algebra of a system with n degrees of freedom includes an infinite-dimensional linear set, which corresponds to an extension of the Hilbert space of the states of the system. This linear set includes a Hilbert space equivalent to that of quantum mechanics and other elements corresponding to functions not belonging to this space and to symbolic functions such as δ and its derivatives. There is no equivalence between this theory and that of the Schwarz distributions, because some of the elements of the above linear set do not correspond to functions or distributions. The geometric algebras lead naturally to the consideration of an isotropic harmonic oscillator with strong spin-orbit coupling. Several new groups of transformations come in into the present theory, some of them constituted by transformations of the classical phase-space. The significance of the affine group for the quantum physics appears very clearly. The second quantization formalisms appear as geometric algebras of separable Hilbert spaces, which correspond to a deeper level of the geometry of the space-time. The ordinary quantum kinematics appears as a link between the micro-geometry of space and the ordinary geometry. Second quantization and the quantum field theory would correspond to the micro-geometry. The relations between physics and geometry discussed in this paper are of a nature essentially different from those of the general theory of relativity. It seems likely that a combination of our geometric-algebraic methods with the general theory of relativity will give a geometrization of both the macro and micro-physics.

D. SETTE. Vedi pag. 434, 447.

A. SICHIROLLO. Vedi pag. 451.

A. STANGHELLINI. Vedi pag. 442.

C. SUCCI. Vedi pag. 451.

L. TAFFARA. Vedi pag. 441.

L. TALLONE. Vedi pag. 446.

E. TARTAGLIONE. Vedi pag. 440.

A. TOMASINI (*Bologna*). – **Emissione multipla nelle reazioni nucleari.**

Si suggerisce l'ipotesi che in nuclei pesanti fortemente eccitati l'emissione contemporanea di più particelle possa competere con l'emissione di una sola particella: sono dedotte espressioni per le probabilità di emissione, con l'ipotesi che i processi possono essere descritti statisticamente. Per energia di eccitazione maggiore di ~ 100 MeV l'emissione di due particelle dovrebbe essere sensibile. Due particelle emesse contemporaneamente devono avere una forte correlazione angolare, ed anche una correlazione energetica: sono favorite emissioni in direzione opposta e con energie uguali. Tali correlazioni sono più vistose nell'emissione di due particelle α : la probabilità che

le due α siano emesse a 180° è $\sim 10^4$ volte la probabilità che siano emesse a 0° . Rispetto a quello che si ha nell'emissione singola, l'emissione multipla dovrebbe abbassare l'energia media delle particelle emesse, e conseguentemente aumentare il numero medio di particelle nella diseccitazione totale; dovrebbe anche aumentare la probabilità di emissione delle α rispetto a quella dei protoni.

A. TOMASINI. Vedi pag. 437.

G. TOMASINI. Vedi pag. 431.

G. TORELLI. Vedi pag. 435.

M. P. TOSI (Palermo). — **Potenziale elettrostatico di celle elementari di reticoli ionici.**

Il calcolo del potenziale elettrostatico in reticoli ionici col metodo di EVJEN ⁽¹⁾ si basa sostanzialmente sul rapido decadimento del potenziale elettrostatico di una cella reticolare con la distanza. Una cella reticolare è neutra ed agisce come un multipolo. La considerazione del carattere tensoriale dei multipoli e l'applicazione del metodo dell'ispezione diretta ⁽²⁾ consentono di stabilire facilmente che il potenziale elettrostatico della cella elementare del reticolo NaCl decade come r^{-7} , mentre il potenziale delle celle elementari dei reticoli tipo CsCl e CaF₂ decade come r^{-5} , e quello delle celle elementari dei reticoli tipo zinc-blenda e cuprite decade come r^{-4} . Le stesse considerazioni consentono di dimostrare che il potenziale elettrostatico dei poliedri di Wigner-Seitz che si introducono nel calcolo del potenziale elettrostatico reticolare col metodo di FRANK ⁽³⁾ decade come r^{-5} , tanto nel caso del reticolo tipo NaCl che nel caso del reticolo CsCl.

⁽¹⁾ H. M. EVJEN: *Phys. Rev.*, **39**, 675 (1932).

⁽²⁾ F. G. FUMI: *Acta Cryst.*, **5**, 44 (1952).

⁽³⁾ F. C. FRANK: *Phil. Mag.*, **51**, 1287 (1950). Per l'estensione del metodo di Frank al reticolo tipo CsCl vedi F. G. FUMI and M. P. TOSI: *The Theory of Ionic Crystals*, da pubblicare su *Solid State Physics* (New York).

C. TRIBUNO. Vedi pag. 449.

G. VANDERHAEGHE (Bruxelles), A. BONETTI (Milano), M. BALDO-CEOLIN, W. D. B. GREENING, S. LIMENTANI and M. MERLIN (Padova). — **The Spin and Parity of τ^+ -Mesons.**

A study has been made of some 400 τ^+ decays found under well defined conditions in two large stacks. The energy and angular distributions of the decay pions have been compared with the theoretical curves given by Dalitz, by Fabri and by Costa and Taffara for various combinations of spin and parity. The problem is of importance in helping to decide if the τ - and θ -mesons must be considered as separate particles, or merely as different decay modes of the same particle.

G. VANDERHAEGHE. Vedi pag. 431.

N. C. VARSHNEYA. Vedi pag. 436, 437.

M. VERDE (*Torino*). - **Urto alle alte energie e fattori di forma nucleari.**

Le figure di diffrazione ottenute nell'urto di elettroni o nucleoni di elevata energia contro nuclei, possono servire a stabilire le distribuzioni di carica coulombiana o nucleare. L'interpretazione teorica viene fatta di solito partendo da una forma particolare per tali distribuzioni e valutando numericamente le sezioni d'urto. Con il proposito di stabilire una teoria generale dei fattori di forma, abbiamo studiato il comportamento delle fasi in un problema di scattering per valori elevati dell'impulso k delle particelle urtanti e per qualunque valore del momento angolare l . Negli sviluppi asintotici, ottenuti facendo uso dell'equazione integrale di Gel'fand e Levitan ⁽¹⁾, il termine di ordine $1/k$ coincide con una formula già nota di Molière ⁽²⁾:

$$\delta(b, k) = - \left(\int_0^{\infty} u(\sqrt{x^2 + b^2}) dx \right) / 2k,$$

essendo b il parametro d'urto: $bk = l + \frac{1}{2}$. Le successive approssimazioni contengono sotto il segno di integrale potenze di U e delle sue derivate. Esse permettono di fare un confronto con il metodo WKB e con le successive approssimazioni di Born. Per l'ampiezza d'urto differenziale $f(\theta)$ viene stabilito il seguente sviluppo:

$$\sqrt{\sin \theta} f(\theta) = \frac{2}{ik} \sum_n^{\infty} S_n(\theta) \left\langle \frac{1}{P_n(k, \theta)} \right\rangle,$$

valido per qualunque θ ad eccezione di un intorno di 180° . $S_n(\theta)$ sono funzioni elementari che si annullano per $\theta = 0$ come θ^n .

$$\left\langle \frac{1}{P_n(k, \theta)} \right\rangle = \int_0^{\infty} \frac{1}{b^{n-1}} t(b, k) \sqrt{\theta} J_n(b, \theta) db \quad n = 0, 1, 2, \dots$$

essendo $t(b, k) = (\exp [2i\delta] + 1)/2i$ l'ampiezza d'urto relativa al momento angolare l . J_n sono le solite funzioni di Bessel di ordine n . Abbiamo studiato il problema di risalire dalla conoscenza delle fasi per un dato k e per tutti i valori di l , alla forma del potenziale che le origina. Se k è sufficientemente elevato in modo da ritenere valido il primo termine dello sviluppo asintotico per δ , si ha la seguente formula di inversione:

$$rU(r) = - \frac{4k}{\pi} \cdot \int_0^{\infty} \int_0^{\infty} \omega \sin \omega r J_0(b\omega) b \delta(b, k) db d\omega.$$

Si discutono alcuni casi particolari.

⁽¹⁾ I. M. GEL'FAND e B. M. LEVITAN: *Izv. Akad. Nauk SSSR.*, **15**, 309 (1951).

⁽²⁾ G. MOLIERE: *Zeits. f. Naturfor.*, **2**, 133 (1942).

L. VERDINI (*Roma*). — Velocità delle onde elastiche e attrito interno nel metacrilato di polimetile.

By means of a dynamical method, the velocity of elastic extensional waves as well as internal friction, have been measured on polymethyl-methacrylate bars, in a temperature range from 20 °C to 100 °C. Bars of rectangular cross-section having a flexural frequency between 580 and 750 Hz have been employed. The transition temperature of the polymer has been detected from the velocity vs. temperature and damping vs. temperature curves. At the transition point, the damping curves show an anomalous horizontal behavior, and in the velocity curves a sudden change in the temperature coefficient is observed. The specimens under measurement have been annealed at different temperatures, and as a consequence of these heat treatments, a series of transition temperatures laying between 52 °C and 63 °C has been found. It may be observed that below the transition point, internal friction increases exponentially with temperature, in agreement with the results obtained in pure metals and alloys. This behaviour seems to agree with a theory due to W. P. MASON, who has shown that the exponential increase of internal friction in solids is due to the breakaways of the dislocations from their impurity pinning points, as a consequence of thermal agitation.

P. VERONESI. Vedi pag. 438.

M. VIGONE. Vedi pag. 446.

P. WALOSCHEK. Vedi pag. 436, 437.

A. WATAGHIN. Vedi pag. 453.

A. WETHERELL. Vedi pag. 451.

J. R. WORMAND. Vedi pag. 451.

G. ZAGO. Vedi pag. 432, 444.

PROPRIETÀ LETTERARIA RISERVATA
